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(71)Applicant : **CANON INC**

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(72)Inventor : **TAKIGUCHI TAKESHI**  
**ARATAIRA FUMIHIRO**  
**HAGINO YOSHIFUMI**  
**OKADO KENJI**  
**IDA TETSUYA**  
**IIDA HAGUMU**  
**KUKIMOTO TSUTOMU**

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**(54) ELECTROPHOTOGRAPHIC CARRIER, ELECTROPHOTOGRAPHIC DEVELOPER  
AND IMAGE FORMING METHOD**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an electrophotographic carrier having high electric charge imparting ability and heat resistance.

SOLUTION: This electrophotographic carrier is a carrier surface-coated with a polyolefin resin layer. At least an ethylene monomer and one or more kinds of  $\leq 4$ C polymerizable monomers each having an unsatd. bond are used in a molar ratio of 99:1 to 1:99 as monomer components constituting the polyolefin resin.

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CLAIMS

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[Claim(s)]

[Claim 1] The carrier for electrophotography characterized by the mole ratio of each monomer using one or more kinds of the polymerization nature monomer which the front face of a carrier is covered with the polyolefine system resin layer, has an ethylene monomer and an unsaturated bond at least as a monomer component which constitutes this polyolefin resin, and consists of four or less carbon atomic numbers at a rate of ethylene monomer:polymerization nature monomer =99:1-1:99.

[Claim 2] The carrier for electrophotography according to claim 1 characterized by carrying out direct polymerization covering of the polyolefin resin on a carrier front face.

[Claim 3] The carrier for electrophotography according to claim 1 or 2 with which this carrier is characterized by having the volume median size of 10-60 micrometers.

[Claim 4] The carrier for electrophotography according to claim 1 to 3 characterized by this carrier having the resistance of 106-1011-ohmcm under the electrical potential difference of 0.5kV - 1kV.

[Claim 5] The carrier for electrophotography according to claim 1 to 4 characterized by this carrier having the value whose saturation magnetization is 15-85Am<sup>2</sup>/kg to the impression magnetic field of 79.6 kA/m (1000 oersteds).

[Claim 6] The developer for electrophotography characterized by the mole ratio of each monomer using one or more kinds of the polymerization nature monomer which the front face of this carrier is covered with the polyolefine system resin layer, has an ethylene monomer and an unsaturated bond at least as a monomer component which constitutes this polyolefin resin in the developer for electrophotography which has a toner and a carrier at least, and consists of four or less carbon atomic numbers at a rate of ethylene monomer:polymerization nature monomer =99:1-1:99.

[Claim 7] The developer for electrophotography according to claim 6 characterized by carrying out direct polymerization covering of the polyolefin resin on a carrier front face.

[Claim 8] The developer for electrophotography according to claim 6 or 7 with which this carrier is characterized by having the volume median size of 10-60 micrometers.

[Claim 9] The developer for electrophotography according to claim 6 to 8 characterized by this carrier having the resistance of 106-1011-ohmcm under the electrical potential difference of 0.5kV - 1kV.

[Claim 10] The developer for electrophotography according to claim 6 to 9 characterized by this carrier having the value whose saturation magnetization is 15-85Am<sup>2</sup>/kg to the impression magnetic field of 79.6 kA/m (1000 oersteds).

[Claim 11] The developer for electrophotography according to claim 6 to 10 with which this toner is characterized by having the weighted mean particle size of 1-9 micrometers.

[Claim 12] The developer for electrophotography according to claim 6 to 11 which this toner is a toner for electrophotography which has binding resin and a coloring agent at least, and is characterized by this toner having the acid number 1 - 30 KOHmg/g.

[Claim 13] The developer for electrophotography according to claim 6 to 12 characterized by being in the range whose glass transition temperature of this toner is 45-70 degrees C.

[Claim 14] The developer for electrophotography according to claim 6 to 13 characterized by this toner

being in the range whose temperature which shows the apparent viscosity of 105poise is 80-120 degrees C.

[Claim 15] The developer for electrophotography according to claim 6 to 14 characterized by containing the compound with which this toner consists of a metal which can constitute an anionic polymerization catalyst at least as an external additive.

[Claim 16] The developer for electrophotography according to claim 15 with which the metal which can constitute this anionic polymerization catalyst is characterized by having the value of 1.7Å or more as the bond distance with oxygen.

[Claim 17] The developer for electrophotography according to claim 15 or 16 characterized by this external additive being a metallic oxide with a mean particle diameter of 0.005-0.2 micrometers by which hydrophobing processing was carried out.

[Claim 18] The developer for electrophotography according to claim 15 to 17 with which this external additive is characterized by being an aluminum compound and/or a titanium compound.

[Claim 19] The developer for electrophotography according to claim 6 to 18 characterized by the toner concentration in a developer being 2 - 15 % of the weight.

[Claim 20] It sets on the carrier for electrophotography which has the magnetic ferrite powder by which the front face is covered in the polyolefine system resin layer, and this ferrite powder is the following type (1).

(Fe 2O<sub>3</sub>)<sub>x</sub>(MnO)<sub>y</sub>(A)<sub>z</sub> Formula (1)

[-- the inside of a formula, and A -- Na<sub>2</sub>O, K<sub>2</sub>O, CaO(s) and SrO(s), or those mixture -- being shown -- x, and y and z -- a mole fraction -- being shown -- following condition 0.3 [ and ] -- < -- x < 0.8 and 0.01 -- < -- y < 0.5 and 0 -- < -- z < 0.69 and x+y+z=1 are satisfied.] The carrier for electrophotography characterized by coming out, consisting of ferrite components shown, and carrying out direct polymerization covering of this polyolefin resin layer on a carrier front face.

[Claim 21] x in this type (1), and y and z are the following conditions. 0.3 < x < 0.8 0.01 < y < 0.5 0 < z < 0.69 x+y < 1 Carrier for electrophotography according to claim 20 characterized by satisfying z=1-x-y.

[Claim 22] The carrier for electrophotography according to claim 20 or 21 with which this carrier is characterized by having the volume median size of 10-60 micrometers.

[Claim 23] The carrier for electrophotography according to claim 20 to 22 characterized by this carrier having the resistance of 106-1011-ohmcm under the electrical potential difference of 0.5kV - 1kV.

[Claim 24] The carrier for electrophotography according to claim 20 to 23 characterized by this carrier having the value whose saturation magnetization is 15-85Am<sup>2</sup>/kg to the impression magnetic field of 79.6 kA/m (1000 oersteds).

[Claim 25] In the developer for electrophotography which has a toner and a carrier at least, this carrier has the magnetic ferrite powder covered with the polyolefine system resin layer in the front face, and this ferrite powder is the following formula (1).

(Fe 2O<sub>3</sub>)<sub>x</sub>(MnO)<sub>y</sub>(A)<sub>z</sub> Formula (1)

[-- the inside of a formula, and A -- Na<sub>2</sub>O, K<sub>2</sub>O, CaO(s) and SrO(s), or those mixture -- being shown -- x, and y and z -- a mole fraction -- being shown -- following condition 0.3 [ and ] -- < -- x < 0.8 and 0.01 -- < -- y < 0.5 and 0 -- < -- z < 0.69 and x+y+z=1 are satisfied.] The developer for electrophotography characterized by coming out, consisting of ferrite components shown, and carrying out direct polymerization covering of this polyolefin resin layer on a carrier front face.

[Claim 26] x in this type (1), and y and z are the following conditions. 0.3 < x < 0.8 0.01 < y < 0.5 0 < z < 0.69 x+y < 1 Developer for electrophotography according to claim 25 characterized by satisfying z=1-x-y.

[Claim 27] The developer for electrophotography according to claim 25 or 26 with which this carrier is characterized by having the volume median size of 10-60 micrometers.

[Claim 28] The developer for electrophotography according to claim 25 to 27 characterized by this carrier having the resistance of 106-1011-ohmcm under the electrical potential difference of 0.5kV - 1kV.

[Claim 29] The developer for electrophotography according to claim 25 to 28 characterized by this carrier having the value whose saturation magnetization is 15-85Am<sup>2</sup>/kg to the impression magnetic field of 79.6 kA/m (1000 oersteds).

[Claim 30] The developer for electrophotography according to claim 25 to 29 with which this toner is characterized by having the weighted mean particle size of 1-9 micrometers.

[Claim 31] The developer for electrophotography according to claim 25 to 30 which this toner is a toner for electrophotography which has binding resin and a coloring agent at least, and is characterized by this toner having the acid number 1 - 30 KOHmg/g.

[Claim 32] The developer for electrophotography according to claim 25 to 31 characterized by being in the range whose glass transition temperature of this toner is 45-70 degrees C.

[Claim 33] The developer for electrophotography according to claim 25 to 32 characterized by this toner being in the range whose temperature which shows the apparent viscosity of 105poise is 80-120 degrees C.

[Claim 34] The developer for electrophotography according to claim 25 to 33 characterized by containing the compound with which this toner consists of a metal which can constitute an anionic polymerization catalyst at least as an external additive.

[Claim 35] The developer for electrophotography according to claim 34 with which the metal which can constitute this anionic polymerization catalyst is characterized by having the value of 1.7Å or more as the bond distance with oxygen.

[Claim 36] The developer for electrophotography according to claim 34 or 35 characterized by this external additive being a metallic oxide with a mean particle diameter of 0.005-0.2 micrometers by which hydrophobing processing was carried out.

[Claim 37] The developer for electrophotography according to claim 34 to 36 with which this external additive is characterized by being an aluminum compound and/or a titanium compound.

[Claim 38] The developer for electrophotography according to claim 25 to 37 characterized by the toner concentration in a developer being 2 - 15 % of the weight.

[Claim 39] It sets on the carrier for electrophotography which has the magnetic ferrite powder by which the front face is covered in the polyolefine system resin layer, and this ferrite powder is the following type (2).

(Fe 2O<sub>3</sub>) x(A) y (B) z Formula (2)

[-- a kind or two sorts or more of metallic elements chosen from the group to whom A expresses MgO, Ag<sub>2</sub>O, or MgO+Ag<sub>2</sub>O among a formula, and which B becomes from Li<sub>2</sub>O, MnO<sub>2</sub>, CaO, SrO and aluminum 2O<sub>3</sub>, and SiO<sub>2</sub> -- expressing -- x, and y and z -- a weight ratio -- expressing -- and the following conditions [ ] 0.2<=x<=0.95 -- 0.005<=y<=0.3 and x+y+z<=1 are satisfied.] The carrier for electrophotography characterized by coming out, consisting of ferrite components shown, and carrying out direct polymerization covering of this polyolefin resin layer on a carrier front face.

[Claim 40] The carrier for electrophotography according to claim 39 with which this carrier is characterized by having the volume median size of 10-60 micrometers.

[Claim 41] The carrier for electrophotography according to claim 39 or 40 characterized by this carrier having the resistance of 106-1011-ohmcm under the electrical potential difference of 0.5kV - 1kV.

[Claim 42] The carrier for electrophotography according to claim 39 to 41 characterized by this carrier having the value whose saturation magnetization is 15-85Am<sup>2</sup>/kg to the impression magnetic field of 79.6 kA/m (1000 oersteds).

[Claim 43] In the developer for electrophotography which has a toner and a carrier at least, this carrier has the magnetic ferrite powder covered with the polyolefine system resin layer in the front face, and this ferrite powder is the following formula (2).

(Fe 2O<sub>3</sub>) x(A) y (B) z Formula (2)

[-- a kind or two sorts or more of metallic elements chosen from the group to whom A expresses MgO, Ag<sub>2</sub>O, or MgO+Ag<sub>2</sub>O among a formula, and which B becomes from Li<sub>2</sub>O, MnO<sub>2</sub>, CaO, SrO and aluminum 2O<sub>3</sub>, and SiO<sub>2</sub> -- expressing -- x, and y and z -- a weight ratio -- expressing -- and the following conditions [ ] 0.2<=x<=0.95 -- 0.005<=y<=0.3 and x+y+z<=1 are satisfied.] The developer

for electrophotography characterized by coming out, consisting of ferrite components shown, and carrying out direct polymerization covering of this polyolefin resin layer on a carrier front face.

[Claim 44] The developer for electrophotography according to claim 43 with which this carrier \*\*\*\*\* having the volume median size of 10-60 micrometers.

[Claim 45] Claim 43 characterized by this carrier having the resistance of 106-1011-ohmcm under the electrical potential difference of 0.5kV - 1kV, and the developer for electrophotography given in 44.

[Claim 46] The developer for electrophotography according to claim 43 to 45 characterized by this carrier having the value whose saturation magnetization is 15-85Am<sup>2</sup>/kg to the impression magnetic field of 79.6 kA/m (1000 oersteds).

[Claim 47] The developer for electrophotography according to claim 43 to 46 with which this toner is characterized by having the weighted mean particle size of 1-9 micrometers.

[Claim 48] The developer for electrophotography according to claim 43 to 47 which this toner is a toner for electrophotography which has binding resin and a coloring agent at least, and is characterized by this toner having the acid number 1 - 30 KOHmg/g.

[Claim 49] The developer for electrophotography according to claim 43 to 48 characterized by being in the range whose glass transition temperature of this toner is 45-70 degrees C.

[Claim 50] The developer for electrophotography according to claim 43 to 49 characterized by this toner being in the range whose temperature which shows the apparent viscosity of 105poise is 80-120 degrees C.

[Claim 51] The developer for electrophotography according to claim 43 to 50 characterized by containing the compound with which this toner consists of a metal which can constitute an anionic polymerization catalyst at least as an external additive.

[Claim 52] The developer for electrophotography according to claim 51 with which the metal which can constitute this anionic polymerization catalyst is characterized by having the value of 1.7Å or more as the bond distance with oxygen.

[Claim 53] The developer for electrophotography according to claim 51 or 52 characterized by this external additive being a metallic oxide with a mean particle diameter of 0.005-0.2 micrometers by which hydrophobing processing was carried out.

[Claim 54] The developer for electrophotography according to claim 51 to 53 with which this external additive is characterized by being an aluminum compound and/or a titanium compound.

[Claim 55] The developer for electrophotography according to claim 43 to 54 characterized by the toner concentration in a developer being 2 - 15 % of the weight.

[Claim 56] It is the developer for electrophotography characterized by for this carrier having the polyolefin resin layer which covers a magnetic core material front face and this magnetic core material front face in the developer for electrophotography which has a toner and a carrier at least, and for this toner having the weighted mean particle size of 3-9 micrometers, containing a toner particle with a particle size of 4.00 micrometers or less several 10-70%, and containing the compound of the metal which can constitute an anionic polymerization catalyst at least as an external additive.

[Claim 57] This polyolefin resin layer is a developer for electrophotography according to claim 56 characterized by carrying out direct polymerization covering on this magnetic core material front face.

[Claim 58] This polyolefin resin layer is a developer for electrophotography according to claim 56 or 57 characterized by weight average molecular weight being 5000 or more in the molecular weight distribution acquired from the GPC determination of molecular weight.

[Claim 59] This polyolefin resin layer is a developer for electrophotography according to claim 56 or 57 characterized by weight average molecular weight being within the limits of 7000 thru/or 700000 in the molecular weight distribution acquired from the GPC determination of molecular weight.

[Claim 60] This polyolefin resin layer is a developer for electrophotography according to claim 56 or 57 characterized by weight average molecular weight being within the limits of 30000 thru/or 700000 in the molecular weight distribution acquired from the GPC determination of molecular weight.

[Claim 61] This polyolefin resin layer is a developer for electrophotography according to claim 56 or 57 characterized by weight average molecular weight being within the limits of 50000 thru/or 500000 in the

molecular weight distribution acquired from the GPC determination of molecular weight.

[Claim 62] This polyolefin resin layer is a developer for electrophotography according to claim 58 to 61 characterized by number average molecular weight being within the limits of 2000 thru/or 30000 in the molecular weight distribution acquired from the GPC determination of molecular weight.

[Claim 63] The developer for electrophotography according to claim 56 to 62 with which the metal which can constitute this anionic polymerization catalyst is characterized by having the value of 1.7Å or more as the bond distance with oxygen.

[Claim 64] The developer for electrophotography according to claim 56 to 63 characterized by for this carrier having the volume median size of 10-60 micrometers, and containing the carrier particle 27.5 micrometers or less 1.0 to 80% of the weight.

[Claim 65] The developer for electrophotography according to claim 56 to 64 characterized by this carrier having the resistance of 106-1011-ohmcm under the electrical potential difference of 0.5kV - 1kV.

[Claim 66] The developer for electrophotography according to claim 56 to 65 characterized by this carrier having the value whose saturation magnetization is 15-85Am<sup>2</sup>/kg to the impression magnetic field of 79.6 kA/m (1000 oersteds).

[Claim 67] The developer for electrophotography according to claim 56 to 66 which this toner is a toner for electrophotography which has binding resin and a coloring agent at least, and is characterized by this toner having the acid number 1 - 30 KOHmg/g.

[Claim 68] The developer for electrophotography according to claim 56 to 67 characterized by being in the range whose glass transition temperature of this toner is 45-70 degrees C.

[Claim 69] The developer for electrophotography according to claim 56 to 68 characterized by this toner being in the range whose temperature which shows the apparent viscosity of 105poise is 80-120 degrees C.

[Claim 70] The developer for electrophotography according to claim 56 to 69 characterized by this external additive being a metallic oxide with a mean particle diameter of 0.005-0.2 micrometers by which hydrophobing processing was carried out.

[Claim 71] The developer for electrophotography according to claim 56 to 70 with which this external additive is characterized by being an aluminum compound and/or a titanium compound.

[Claim 72] The developer for electrophotography according to claim 56 to 71 characterized by the toner concentration in a developer being 2 - 15 % of the weight.

[Claim 73] Circulation conveyance of the binary system developer which has a toner and a carrier is carried out by developer support. In the image formation approach of developing the electrostatic latent image currently held in the development field at electrostatic latent-image support with the toner of this binary system developer currently supported by this developer support this carrier It is the image formation approach which has the polyolefin resin layer which covers a magnetic core material front face and this magnetic core material front face, and is characterized by this toner containing the compound of the metal which can constitute an anionic polymerization catalyst at least as an external additive.

[Claim 74] This binary system developer is the image formation approach according to claim 73 characterized by being claim 57 thru/or one developer for electrophotography of 72.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the developer for electrophotography and the image formation approach using the carrier for electrophotography and this carrier which especially improved an electrification property, endurance, and an image property remarkably about the carrier for developers and developer which are used for developing an electric latent image or a magnetic latent image in a xerography or electrostatic printing.

[0002]

[Description of the Prior Art] Although the carrier which constitutes a binary system developer is divided roughly into a conductive carrier and an insulating carrier and the iron powder which is not oxidized [ oxidation or ] is usually used as a conductive carrier, in the developer which uses this iron powder carrier as a component, the frictional electrification nature of a toner is unstable, and the visible image formed by the developer has the fault of being easy to generate fogging. That is, since it follows on use of a developer and a toner particle is adhered and accumulated in the front face of an iron powder carrier particle (toner SUPENTO), the image concentration of the visible image which the electric resistance of a carrier particle rises, and a bias current falls, and moreover becomes unstable [ frictional electrification nature ], consequently is formed falls, and fogging increases. Therefore, if it prints continuously with electrophotography equipment using the developer containing an iron powder carrier, since a developer will deteriorate in a small number of time, it is necessary to exchange developers at an early stage, and cost will become high after all.

[0003] Moreover, the carrier which covered with resin etc. to homogeneity the front face of the core material of the carrier which generally consists of ferromagnetics, such as iron, nickel, and a ferrite, as an insulating carrier is typical. In the developer using this carrier, compared with the case where it is a conductive carrier that a toner particle welds to a carrier front face, it is remarkably few, it is easy for coincidence to control the frictional electrification nature of a toner and a carrier, it excels in endurance, and there is an advantage of being suitable for especially high-speed electrophotography equipment, at the point that a use life is long.

[0004] Although there are various properties demanded from an insulating carrier, electrification nature suitable as an important property, shock resistance, abrasion resistance, the good adhesion of a core and covering material, the homogeneity of charge distribution, etc. can be mentioned especially.

[0005] If many above-mentioned demand characteristics are taken into consideration, the insulating carrier used conventionally has left the problem which should still be solved, and, for the moment, the perfect thing is not known. For example, the example using acrylic resin etc. as a cladding material of a carrier is indicated by JP,47-13954,A, JP,60-208765,A, etc., and the example using polyolefine system resin as a cladding material of a carrier is indicated by JP,52-154639,A, JP,54-35735,A, etc. Moreover, as what especially molecular weight is stated to, it is indicated by JP,60-208767,A etc. and it is known that the electrification nature of the carrier covered by carrying out fixed management of the molecular weight will be stable. However, in order to make covering resin adhere to a carrier core material, to

make resin adhere to a core material stably and to give sufficient electrification nature and endurance even if it is easy to be influenced of the environment which covers conditions, humidity, etc. of equipment and manages them severely, the present condition is that there is nothing that can still be satisfied.

[0006] Furthermore, although the attempt in which the high definition of a copying machine and the demand of high-definition-izing are increasing in the commercial scene, will make particle size of a toner fine in the technical field concerned, and high definition-ization will be attained in recent years is made. If the particle size of a toner becomes fine, the surface area per unit weight will increase, and we are in the inclination for an electrification rate to become slow in addition to the amount of electrifications of a toner becoming large, and are just going to be anxious about durable degradation like image \*\*\*\*\*, and fogging and toner scattering.

[0007] That is, in the development of the electrostatic latent image currently held at the electrostatic latent-image supporter, it is mixed with the carrier which is a large drop child comparatively, and a toner is used as a developer for electrophotography. By mutual contact friction, the presentation of both toner and carrier is chosen so that a toner may be tintured with a polarity opposite to the charge on a photoconduction layer. As a result of both contact friction, a carrier makes a toner adhere to a front face electrostatic, conveys the inside of a developer as a developer, and supplies a toner on the photoconduction layer of an electrostatic latent-image supporter.

[0008] However, if several multi-sheet continuation copy is performed by the electronic reproducing unit using such a developer, in early stages, an image with clear and good image quality will be obtained, but there is much fogging and it serves as a scarce image at gradation nature and clear nature as the number of copies increases.

[0009] In addition to the toner of the un-proper amount of electrifications participating in development, the standup of the prompt frictional electrification between a supply toner and the carrier in a developer worsens, and this is for the electrification grant ability of a carrier to fall by degradation of toner SUPENTO or coat material, and it becomes remarkable [ this phenomenon ], so that the particle size of the toner used is fine.

[0010] So, in JP,2-281280,A, the narrow carrier of particle size distribution which controlled the abundance of fines and the abundance of coarse powder is proposed, and the carrier whose development property improved is attained. The further minor diameter-ization of a carrier is also tried further again for the purpose of improvement in the development effectiveness at the time of toner use of a fine particle size. However, in such a carrier, it is difficult for the actual condition for sufficient quality which can cope with the amount change of electrifications by the environment of a toner or durability not to be acquired, but to attain all high image concentration, high definition, the good fogging prevention, and carrier antisticking.

[0011] On the other hand, amelioration from a toner side is also performed positively that various problems like the above should be solved.

[0012] The fluidity of a toner is raised and carrying out addition mixing of the silica impalpable powder at toner powder is proposed by JP,46-5782,A, JP,48-47345,A, and JP,48-47346,A as a means to attain the standup of the prompt frictional electrification between a supply toner and the carrier in a developer.

[0013] However, the additive which can give sufficient fluidity to such toners needs to have a very fine particle size, and since wear of the carrier cladding material by the carrier contamination (the so-called carrier SUPENTO) and the additive which are called adhesion of the additive to carrier coat material will be easy to be generated as a result and the electrification grant ability of a carrier falls, fogging serves as many images lacking in gradation nature and clear nature as the number of copies increases.

[0014] Thus, the actual condition is that the developer with which it is satisfied with of the standup of prompt electrification and control of carrier SUPENTO, and may be satisfied of the high definition which does not have high image concentration and fogging to prolonged use enough is not yet obtained.

[0015]

[Problem(s) to be Solved by the Invention] The main purposes of this invention are to offer the good carrier for electrophotography, the developer for electrophotography, and the image formation approach

of the endurance improved in many conventional faults like the above especially the electrification property under various environments, a mechanical strength, adhesion with a core material, and SUPENTO-proof nature.

[0016] Moreover, the purpose of this invention has the good endurance of toner imprint nature, and it is to offer the developer for electrophotography and the image formation approach that image quality degradation of the highlights section is not seen in long-term use.

[0017] Furthermore, it is in offering the developer for electrophotography and the image formation approach which a blemish does not generate on a photo conductor front face in long-term use.

[0018]

[Means for Solving the Problem] As for this invention, the front face of a carrier is covered with the polyolefine system resin layer. At least one or more kinds of the polymerization nature monomer which has an ethylene monomer and an unsaturated bond and consists of four or less carbon atomic numbers as a monomer component which constitutes this polyolefin resin the mole ratio of each monomer -- ethylene monomer: -- it is related with the developer for electrophotography which has the carrier for electrophotography and this carrier which are characterized by the thing of polymerization nature monomer =99:1-1:99 which it comes out comparatively and is used ("this invention 1" means this invention below.) .

[0019] Moreover, for this invention, it sets on the carrier for electrophotography which has the magnetic ferrite powder by which the front face is covered in the polyolefine system resin layer, and this ferrite powder is the following type (1).

(Fe 2O<sub>3</sub>) x(MnO)y (A) z Formula (1)

[-- the inside of a formula, and A -- Na<sub>2</sub>O, K<sub>2</sub>O, CaO(s) and SrO(s), or those mixture -- being shown -- x, and y and z -- a mole fraction -- being shown -- following condition 0.3 [ and ] -- < -- x< 0.8 and 0.01 -- < -- y< 0.5 and 0 -- < -- z< 0.69 and x+y+z<=1 are satisfied.] It comes out, consists of ferrite components shown, and is related with the developer for electrophotography which has the carrier for electrophotography and this carrier which are characterized by carrying out direct polymerization covering of this polyolefin resin layer on a carrier front face ("this invention 2" means this invention below.).

[0020] Furthermore, for this invention, it sets on the carrier for electrophotography which has the magnetic ferrite powder by which the front face is covered in the polyolefine system resin layer, and this ferrite powder is the following type (2).

(Fe 2O<sub>3</sub>) x(A) y (B) z Formula (2)

[-- a kind or two sorts or more of metallic elements chosen from the group to whom A expresses MgO, Ag<sub>2</sub>O, or MgO+Ag<sub>2</sub>O among a formula, and which B becomes from Li<sub>2</sub>O, MnO<sub>2</sub>, CaO, SrO and aluminum 2O<sub>3</sub>, and SiO<sub>2</sub> -- expressing -- x, and y and z -- a weight ratio -- expressing -- and the following conditions [ ] 0.2<=x<=0.95 -- 0.005<=y<=0.3 and x+y+z<=1 are satisfied.] It comes out, consists of ferrite components shown, and is related with the developer for electrophotography which has the carrier for electrophotography and this carrier which are characterized by carrying out direct polymerization covering of this polyolefin resin layer on a carrier front face ("this invention 3" means this invention below.).

[0021] In the developer for electrophotography with which this invention has a toner and a carrier at least furthermore, this carrier It has the polyolefin resin layer which covers a magnetic core material front face and this magnetic core material front face. This toner has the weighted mean particle size of 3-9 micrometers, and contains a toner particle with a particle size of 4.00 micrometers or less several 10-70%. It is related with the developer for electrophotography characterized by containing the compound of the metal which can constitute an anionic polymerization catalyst at least as an external additive ("this invention 4" means this invention below.). .

[0022] Furthermore, this invention carries out circulation conveyance of the binary system developer which has a toner and a carrier by developer support. In the image formation approach of developing the electrostatic latent image currently held in the development field at electrostatic latent-image support with the toner of this binary system developer currently supported by this developer support this carrier

It has the polyolefin resin layer which covers a magnetic core material front face and this magnetic core material front face. It is related with the image formation approach characterized by this toner containing the compound of the metal which can constitute an anionic polymerization catalyst at least as an external additive ("this invention 5" means this invention below.).

[0023]

[Embodiment of the Invention] Although the carrier of this invention 1 is covered with polyolefine system resin, the description is in the resin presentation.

[0024] In the case of the carrier which covered only polyethylene resin, although SUPENTO-proof nature improves, in a polyethylene resin layer, there are few sites which can carry out the trap of the charge. For this reason, when it is used for the developer for electrophotography, the electrification grant ability of TONAHE is small, and in addition to good electrophotographic properties not being obtained, it is easy to generate problems, such as fogging, at the time of prolonged use, since the electrification rate is slow. As a monomer component which constitutes resin here, by using together with an ethylene monomer one or more kinds of polymerization nature monomers which have an unsaturated bond and consist of four or less carbon atomic numbers, the electrification grant ability and the electrification rate of a carrier which carried out the coat rise, and it becomes possible to improve endurance greatly.

Although it is not yet clear about this reason, when the negative electrification grant capacity of \*\* RIKYARIA becoming high at that electron when a methyl group's exists, and an unsaturated bond remain, in the monomer part used together with ethylene, it is imagined that that part serves as a trap site of a charge, and quick electrification by the forward electrification capacity and the hopping of a carrier improves. Moreover, although polyethylene resin becomes inadequate [ adhesion with a carrier core material ] when it is independently used by having a certain amount of crystallinity, by using other monomers together, the crystallinity is checked and it is also considered that the adhesion with a carrier core material improved.

[0025] Here, when the carbon number of the monomer component used together is five or more, since reactivity falls, the reinforcement of covering resin falls, and sufficient endurance is not acquired. It is important in that case to use the mole ratio of each monomer at a rate of ethylene monomer:polymerization nature monomer =99:1-1:99. When the sufficient electrification grant ability and sufficient quick electrification of TONAHE are not acquired when an ethylene monomer is used so much more than this range, and an ethylene monomer is used in the small quantity below this range, SUPENTO-proof nature falls and sufficient endurance is not acquired.

[0026] In the carrier of this invention 1, it is one of the more desirable use gestalten to combine polyolefin resin with the covering approach which carries out direct polymerization covering on a carrier front face. When the coat carrier which only covered polyolefin resin with the spray-drying method or the dry type coat method is used for the developer for electrophotography, it is easy to generate peeling of covering resin, the fall of the amount of electrifications, deterioration of image quality, etc. when [ appropriate ] it is alike and direct polymerization covering of the polyolefin resin is carried out on a carrier front face in this invention 1, the adhesion of covering resin and a carrier core material improves further, and the endurance of a good electrification property improves remarkably. About this, it becomes quick [ this invention person etc. / the charge transfer between covering resin, not only the charge transfer between toners but covering resin, and a carrier core material ], and if the \*\* RIKYARIA engine performance pulls to both synergistic effect, it is interpreted as that in which the engine performance as a developer for electrophotography increased greatly.

[0027] In addition, although indicated in JP,2-187770,A or JP,4-70853,A about the carrier which carried out direct polymerization formation of the polyolefin resin layer on the core material front face, as for the carrier of this invention 1 which the contents use a specific other type monomer together positively in the amount of specification about an independent monomer presentation, and is raising an electrification property and endurance, the contents differ.

[0028] The carrier of this invention 2 has the big description in the core material presentation, although direct polymerization formation of the polyolefine system resin layer is carried out on the core material front face.

[0029] First, Fe 2O<sub>3</sub> is a component required in order to acquire proper magnetic properties, and can acquire good image quality in the magnetic brush development approach especially.

[0030] Although it is effective for controlling the electrification grant ability under highly humid to make the oxide of alkali metal or alkaline earth metal contain, maintaining carrier resistance within proper limits, the effectiveness increases by leaps and bounds by using together especially with MnO.

[0031] However, according to a detailed examination of this invention person etc., it became clear that effectiveness is looked at by only the metal atom in which all alkali metal or alkaline earth metal do not have effectiveness, and have the physical-properties value of a certain specification within the limits.

[0032] Namely, in order for each presentation component to dissolve and suit mutually, to constitute a crystal lattice and to become controllable [ electric resistance and the amount of electrifications ] The result which the range of a proper ionic radius is required in the metal to contain, and this invention person etc. examined wholeheartedly, In the ionic radius of Li<sup>+</sup>, Be<sup>2+</sup>, and Mg<sup>2+</sup>, are smaller than the proper range. Moreover, for it being larger than the proper range, becoming low resistance from the carrier resistance range desirable in any case, and using as a carrier for electrophotography at the ionic radius of Rb<sup>+</sup> and Cs<sup>+</sup>, it was unsuitable. Moreover, it is required for control of the amount of electrifications for metaled ionization potential's being low and an atomic high condition to exist, and it is also clear that the high amount of electrifications is not obtained even if it makes the metal which does not have a high valence any more like Ba<sup>2+</sup> contain.

[0033] It is considered to be one of the causes from the thing with a certain amount of rheostatic control possible from the ability to take [ although it is not clear about especially the reason high effectiveness is acquired when MnO is made to live together as mentioned above, Mn oxide dissolves mutually with Fe 2O<sub>3</sub>, and ] Spinel structure and for which ionization potential can take a valence state high moreover at slight lowness to have comparatively high electrification capacity. That is, in order that grids structure or a metallic valence condition may carry out a perturbation to each other mutually by making MnO, alkali metal, or alkaline earth metal live together, it is thought that it raises each effectiveness for each other in multiplication.

[0034] As a ferrite carrier which uses MnO as an indispensable component, the ferrite carrier which uses MnO and MgO as an indispensable component is proposed by JP,58-123552,A, JP,59-111159,A, and JP,6-23866,B, and the ferrite carrier which uses MnO and Li<sub>2</sub>O as an indispensable component is proposed by JP,58-215664,A, JP,59-111926,A, and JP,62-297857,A. However, even if it made MgO or Li<sub>2</sub>O coexist with MnO, the effectiveness of the field of resistance adjustment was inadequate according to this invention person's etc. examination. This is considered because it has shifted to constituting a stable and uniform crystal lattice from Li<sup>+</sup> or Mg<sup>2+</sup> from the range of a proper ionic radius as mentioned above.

[0035] Moreover, in JP,6-23866,B, the proposal of a purport which may make the metal like Cu, Zn, and Co live together further during a ferrite presentation in addition to MnO and MgO is made. However, even if it made such metals contain according to this invention person's etc. examination, it became clear [ that it is not easy ] to heighten the electrification grant capacity of a carrier.

[0036] Correlation is looked at by the metaled ionization potential and the electrification grant capacity of a carrier which are generally contained in a carrier, and this is understood from it being hard to carry out forward electrification of the carrier, so that ionization potential is large. That is, when the ionization potential of the metal contained during the ferrite presentation indicated by JP,6-23866,B and the metal contained in a magnetic ferrite component in this invention is compared, it is the following relation Cu. Zn Co>Na K calcium Sr ( size <- ionization potential -> smallness )

It comes out and becomes rank as shown, and when Na, K, calcium, and Sr of ionization potential are smaller and it contains in a carrier as compared with Cu, Zn, and Co, it is thought that it acts so that forward electrification may be carried out more.

[0037] The magnetic ferrite component used in this invention 2 is the following type (1).

(Fe 2O<sub>3</sub>)<sub>x</sub>(MnO)<sub>y</sub> (A)<sub>z</sub> Formula (1)

[-- the inside of a formula, and A -- Na<sub>2</sub>O, K<sub>2</sub>O, CaO(s) and SrO(s), or those mixture -- being shown -- x, and y and z -- a mole fraction -- being shown -- following condition 0.3 [ and ] -- <- x< 0.8 and 0.01

-- < --  $y < 0.5$  and  $0 < -- z < 0.69$  and  $x+y+z \leq 1$  are satisfied.] It is come out and shown.

[0038] It sets at an above-mentioned ceremony (1), and  $x$ , and  $y$  and  $z$  are the following conditions preferably.  $0.3 < x < 0.8$   $0.01 < y < 0.5$   $0 < z < 0.69$   $x+y < 1$  Satisfying  $z=1-x-y$  more -- desirable --  $0.4 < x < 0.8$   $0.02 < y < 0.3$   $0 < z < 0.3$  Although it is desirable in the point of improvement in the electrification capacity of a carrier to satisfy  $x+y+z \leq 1$  Other metallic elements are aimed at the coalescence prevention or particle-size-distribution adjustment at the time of adjustment of the diameter of crystal grain of a magnetic carrier core material particle, and baking in [ which does not bar the effectiveness which the above-mentioned magnetic ferrite component has in this invention ] 0.03 or less mole ratios. You may make it contain with gestalten, such as a hydroxide, an oxide, a sulfide, or an acid compound salt, in a magnetic ferrite component.

[0039] In the above-mentioned formula (1), since it becomes high [ resistance ] in 0.3 or less mole ratios very much [  $x$  ], control of resistance becomes difficult, and since magnetic properties fall in 0.8 or more mole ratios, when  $x$  uses for the magnetic brush developing-negatives method, good image quality is hard to be acquired. It will be difficult for  $y$  to control both carrier resistance and magnetic properties by 0.01 or less mole ratios in the proper range, and magnetic properties will fall [  $y$  ] by 0.5 or more mole ratios. When  $z$  is zero mol (i.e., when (A) is not contained) and it especially combines with the diameter toner of a particle, electrification capacity declines and it is hard coming to maintain endurance.

[0040] It is also the big description to raise the endurance of an electrification property and imprint nature remarkably by furthermore combining polyolefin resin with the covering approach which carries out direct polymerization covering on a carrier front face to the above-mentioned carrier core material in this invention 2.

[0041] Although SUPENTO-proof nature improves, since the site which carries out the trap of the charge does not exist in a polyethylene resin layer in the case of the carrier which carried out direct polymerization formation of the polyethylene resin layer on the core material front face, When it is used for the developer for electrophotography, since [ that the electrification grant ability of TONAHE is small ] the electrification rate is slow, the amount distribution of electrifications of a toner broadcloth-izes, the imprint nature of a toner falls, the image quality of the highlights section becomes an ill-behaved \*\*\*\* thing, and it is easy to generate problems, such as fogging, at the time of further prolonged use. In addition, when the resin used as a cladding material has a certain amount of crystallinity, peeling of a resin layer etc. tends to take place with prolonged use, and since adhesion with a carrier core material is inadequate, since the charge transfer rate between a core material and resin is also slow, the fall of an electrification property is not avoided with prolonged durability.

[0042] However, when direct polymerization formation of the polyolefin resin layer is carried out on the carrier core material front face which consists of the above-mentioned ferrite presentation, wear of not only SUPENTO-proof nature but an enveloping layer, peeling, and electrification grant ability, an electrification rate and extensive amelioration of the amount distribution of electrifications are still attained.

[0043] As this reason, it guesses as follows. In the carrier of this invention 2, a reduction operation is considered to be a strong thing according to negative electrification grant ability being high. Therefore, when a reduction polymerization reaction advances on a carrier front face, it activates more and the capacity of a catalyst may serve as molecular weight distribution strong against wear or peeling in the formed covering resin.

[0044] Moreover, own electrification grant ability of a carrier core material is considered to be what also has the high charge impregnation capacity of TONAHE through a polymerization catalyst and a polyolefin resin layer according to a high thing.

[0045] The effectiveness mentioned above was remarkable further again, especially when A in a formula (1) was calcium or Sr.

[0046] this invention person etc. has considered as follows as this reason.  $Ti^{4+}$  and  $Mg^{2+}$  contain in the catalyst for polyolefine polymerizations used for processing on the front face of a carrier in this invention 2. When alkaline earth metal contains during the presentation of the above-mentioned carrier core material, the adhesion to the carrier core material front face of the polyolefin resin by which the

compatibility with Mg atom which is the same alkaline earth metal improved in the surface treatment of a carrier, the atomic permutation took place in part, consequently polymerization covering was carried out also improves sharply, and it is thought that the charge transfer rate between an enveloping layer and a carrier core material was also improved further remarkably.

[0047] In addition, it is also guessed that the catalytic activity at the time of a polymerization changed with interactions with this core material constituent further, and the molecular weight distribution of the polyolefin resin formed became the adhesion on the front face of a core material and an abrasion resistance pan with the proper thing by SUPENTO-proof nature.

[0048] The carrier of this invention 3 has the big description in the core material presentation, although direct polymerization formation of the polyolefine system resin layer is carried out on the core material front face.

[0049] The magnetic ferrite component used in this invention 3 is the following type (2).

$(\text{Fe } 2\text{O}_3)_x(\text{A})_y(\text{B})_z$  Formula (2)

[-- a kind or two sorts or more of metallic elements chosen from the group to whom A expresses MgO, Ag<sub>2</sub>O, or MgO+Ag<sub>2</sub>O among a formula, and which B becomes from Li<sub>2</sub>O, MnO<sub>2</sub>, CaO, SrO and aluminum 2O<sub>3</sub>, and SiO<sub>2</sub> -- expressing -- x, and y and z -- a weight ratio -- expressing -- and the following conditions [ ]  $0.2 \leq x \leq 0.95$  --  $0.005 \leq y \leq 0.3$  and  $x+y+z \leq 1$  are satisfied.] It is come out and shown.

[0050] First, Fe 2O<sub>3</sub> is a component required in order to acquire fitness magnetic properties and resistive characteristic, and can acquire good image quality in the magnetic brush development approach especially.

[0051] In the above-mentioned formula (2), when x is less than 0.2, magnetic properties become low, it is easy to produce the blemish on the carrier adhesion at the time of development, or the front face of a photo conductor, when x exceeds 0.95, resistance of a ferrite core material tends to become low, and deterioration of the amount of electrifications and image quality is seen. When fitness resistance and magnetic properties are hard to be acquired when y is less than 0.005, and y exceeds 0.3, it may be able to stop being able to attain homogenization and balling-up on a carrier particle front face. moreover, x+y+z does not necessarily need to be 1, and, other than this, may be boiled, and other metallic oxides or compounds may contain it in the range which does not spoil the property of a carrier core material.

[0052] As an A component used suitable for this invention 3, it is the solubility of 0.62mg / 100ml MgO, and the ferrite particle that similarly contains Ag(1.74mg / 100ml)<sub>2</sub>O, and more preferably, since surface homogenization and balling-up contain easy and moderate moisture, the ferrite particle which contains MgO 0.5 to 30% of the weight by oxide conversion at least in respect of the resistance stability of a core material is desirable.

[0053] Moreover, as a B component used suitable for this invention 3, MnO<sub>2</sub>, CaO, aluminum 2O<sub>3</sub>, and SiO<sub>2</sub> with a small resistance fall are more preferably mentioned also at the time of high-voltage impression, and it is a point concordance easy [ with a supply toner ], and MnO<sub>2</sub> and CaO are desirable, although Li<sub>2</sub>O, MnO<sub>2</sub>, CaO, SrO and aluminum 2O<sub>3</sub>, and SiO<sub>2</sub> are mentioned still more preferably.

[0054] It is also the big description to have combined polyolefin resin with the covering approach which carries out direct polymerization covering on a carrier front face to the above-mentioned carrier core material in this invention 3 furthermore.

[0055] Although SUPENTO-proof nature improves, since the site which carries out the trap of the charge does not exist in a polyethylene resin layer in the case of the carrier which carried out direct polymerization formation of the polyethylene resin layer on the core material front face, When it is used for the developer for electrophotography, since [ that the electrification grant ability to the additive of a toner and superfines is small ] the electrification rate is slow, it is difficult to electrify each additive in homogeneity, and since a non-imprinted additive is generated so much at the time of an imprint, generating of the blemish on the front face of a photo conductor is not avoided.

[0056] However, when direct polymerization formation of the polyolefin resin layer is carried out on the carrier core material front face which consists of the above-mentioned ferrite presentation, the electrification grant ability to a metallic oxide improves, and when a non-imprinted additive decreases

sharply, it becomes possible to control generating of the blemish on the front face of a photo conductor. [0057] Although it is [ current ] under elucidation about this reason, to one, the metallic element which constitutes the ferrite component concerning this invention 3 can consider that a charge transfer reaction with the metallic oxide added by the toner is quick. The hygroscopic effectiveness of a configuration metallic element is also considered further again. Namely, since MgO or Ag<sub>2</sub>O contained to a ferrite particle has moderate hygroscopicity, In case a carrier core material front face is processed by the polyolefine polymerization catalyst, catalytic activity is moderately eased by the adsorption moisture. The molecular weight of the polyolefin resin covered or the clearance between polymer chains will become proper to migration of the charge between a carrier front face and the additive for toners, Furthermore, adsorption moisture may promote the charge transfer reaction rate between a core material front face and an enveloping layer, and may be raising the electrification rate of the additive for toners. [0058] In addition, although containing a part of above-mentioned general formula (2) as a carrier constituent also in JP,2-33159,A is indicated, in this invention 3, the description is to carry out the amount content of specification of the metallic oxide which has specific solubility, and carry out direct polymerization formation of the polyolefin resin layer on a carrier core material front face, consequently extensive amelioration of the life of not only the endurance of a carrier but a photo conductor is enabled, and it differs from said invention.

[0059] Moreover, as a ferrite carrier containing MgO, although indicated by JP,59-111159,A, JP,58-123551,A, JP,55-65406,A, etc., for example, these are not what meant the interaction with surface coating resin, and differ in this invention 3.

[0060] Furthermore, although JP,2-33159,A has the publication which may make MgO contain, like this invention 3, MgO is adopted positively, a carrier core material front face is controlled, and there is no suggestion which is going to raise reactivity and they differs in this invention 3 too.

[0061] In the developer of this invention 4, it has the toner and the carrier at least, and the carrier has the polyolefin resin layer which covers a magnetic core material front face and this magnetic core material front face, and it is characterized by a toner containing the compound of the metal which can constitute an anionic polymerization catalyst at least as an external additive.

[0062] Although it is one of the desirable gestalten to use for the developer of this this invention 4 the carrier explained by above-mentioned this invention 1 thru/or 3, it is not necessarily restricted to these carriers.

[0063] In this invention, it is desirable from the endurance as a developer improving by leaps and bounds by using that by which direct polymerization formation of the polyolefine system resin layer was carried out on the carrier core material front face as a carrier. Since resin covering of the whole carrier front face is carried out at homogeneity, this is [ wear of not only the SUPENTO-proof nature but an enveloping layer, prevention of peeling, and ] for electrification grant ability and an electrification rate to improve greatly further.

[0064] In the case of the amount of macromolecules of 50000-500000, in the molecular weight distribution acquired from the GPC determination of molecular weight of a polyolefin resin layer, molecular weight is remarkable [ this effectiveness ] in 7000-700000, and a pan to 30000-700000, and a pan especially more preferably 5000 or more weight average molecular weight. Furthermore, it is desirable in that case that number average molecular weight is in the range of 2000-30000 from a viewpoint of the adhesion to the carrier core material front face of polyolefin resin.

[0065] That is, an enveloping layer will tend to become uneven, if with a weight average molecular weight of 5000 or more polyolefin resin is dissolved [ as opposed to / generally / an organic solvent ] although it is expected that SUPENTO-proof [ endurance and ] nature improves more when it applies to a carrier front face since membranous reinforcement is high when with a weight average molecular weight of 5000 or more polyolefin resin is membrane-formation-ized, and it excels in a mold-release characteristic, wet spreading of \*\*\*\*\* and this solution is carried out on a carrier front face and an enveloping layer is formed. However, since the polyolefin resin layer of the amount of macromolecules can be formed in homogeneity when direct polymerization is carried out on a carrier front face, endurance will improve remarkably.

[0066] Since the reinforcement of the membrane-formation-ized film falls and a mold-release characteristic falls when the number average molecular weight of polyolefin resin is less than 2000, when it applies to a carrier front face, endurance and SUPENTO-proof nature tend to fall, and when number average molecular weight exceeds 30000, the adhesion of the polyolefin resin to a carrier core material front face falls, and it becomes easy to produce exfoliation of the enveloping layer of the polyolefin resin covered on the carrier core material front face.

[0067] In these this inventions, the approach indicated by JP,60-106808,A or JP,60-106809,A can be used as an approach for manufacturing a carrier, for example. Moreover, it is one of the use gestalten also with also raising more the adhesion of a polyolefin resin layer and a carrier core material, and desirable also using the carrier after covering, being possible and conglobating by heat-treatment further by adjusting molecular weight suitably from manufacture conditions.

[0068] On the other hand, the polyolefin resin covering carrier of this invention became clear [ that the electrification property which was excellent when especially carrier particle size was small is also shown ]. Although frictional electrification with a toner or an additive becomes advantageous since carrier surface area will increase if carrier particle size generally becomes small, conversely, it becomes difficult to carry out resin covering at homogeneity, and problems, such as a fall of the imprint nature by partial poor electrification and fogging, tend to generate the whole carrier front face. However, in the carrier of this invention, according to it being possible to cover the whole carrier front face to homogeneity, even when carrier particle size is small, a good electrification property is shown.

Therefore, even when it is difficult to electrify each additive particle in homogeneity like [ at the time of the toner use with a fine particle size which contained the additive so much ], there is little generating of the particle of poor electrification, and it is possible to obtain a high definition image.

[0069] Thus, the carrier of this invention becomes able [ specific surface area ] to use it combining the toner of the large diameter of a granule in order to show the electrification property which was excellent even if it used it with a small particle size.

[0070] Although high definition-ization can be attained when a toner with a particle size fine like point \*\* is used, on the other hand, toner specific surface area increases, and it is in the inclination for an electrification rate to become slow in addition to the amount of electrifications of a toner becoming large, and is easy to generate durable degradation like image \*\*\*\*\*, and fogging and toner scattering. In addition, since toner specific surface area increases, contact time with a carrier becomes long, and there is a trouble of becoming easy to produce carrier SUPENTO.

[0071] However, by combining with a carrier with a small particle size which takes the configuration of this invention, carrier SUPENTO is not seen, and each toner particle can be electrified in homogeneity, durable degradation like image \*\*\*\*\*, and fogging and toner scattering can be prevented, and a high definition image can be obtained over a long period of time.

[0072] As this proper carrier grain size, that whose volume median size is 10-60 micrometers is good, and if it is 10-40 micrometers, it is still more desirable. If it becomes smaller than this range, the fluidity of a developer will fall, since the load at the time of circulation of the developer in a development counter becomes large, a developer becomes being easy to deteriorate, and if this range is exceeded, electrification rate sufficient at the time of the diameter toner use of a granule will be hard to be obtained. It is more desirable to contain the particle 27.5 more micrometers or less 1.0 to 80% of the weight. By this particle-size-distribution configuration, even when SUPENTO [ a carrier front face ] to some extent, a good electrification property can be maintained, and endurance improves further. Since the apparent density of a developer will increase at the time of development in addition to becoming easy to generate carrier adhesion if extensive amelioration of endurance is difficult for a particle 27.5 micrometers or less at less than 1.0% and it exceeds 80 % of the weight, the load at the time of circulation of the developer in a development counter becomes large too, and a developer becomes easy to deteriorate.

[0073] It sets on the carrier of this invention further again, the resistance under the electrical potential difference of 0.5kV - 1kV is 106-1011-ohmcm, and when it has the value whose saturation magnetization is 15-85Am<sup>2</sup>/kg to a 79.6kA [ /m ] (1000 oersteds) impression magnetic field, the

endurance as a developer improves more. The toner which is hard to be developed since the alternative development of the toner which is easy to be developed by descent of the development electric field between a photo conductor and developer support will become easy to take place if carrier resistance becomes higher than 1011-ohmcm is accumulated, and it becomes easy for \*\* RIKYARIASUPENTO to generate for this accumulated toner carrying out long duration stay on a carrier. On the other hand, when carrier resistance is lower than 106-ohmcm, even if the image quality acquired deteriorates greatly and uses the toner of the diameter of a granule, the effectiveness of the high-definition-izing is not demonstrated enough. Moreover, when the saturation magnetization to the impression magnetic field of 79.6 kA/m (1000 oersteds) is larger than 85Am<sup>2</sup>/kg, while endurance falls when a developer tends to deteriorate at the time of developer churning near the developer support, it becomes inadequate when smaller than 15Am<sup>2</sup>/kg mixing a supply toner and the endurance of an electrification property falls, carrier development and the so-called carrier adhesion occur.

[0074] As a means to obtain the carrier which has the above-mentioned resistance range, the technique of arbitration, such as adjustment by the carrier core material, adjustment from the amount of cladding material covering, or adjustment that contains [ make ] a conductive additive in an enveloping layer, can be used. If it is carbon black, TiO<sub>2</sub>, SnO<sub>2</sub> grade, and the ingredient that makes resistance of \*\* RIKYARIA fall to adding as a conductive additive to apply, it is possible to choose it as arbitration.

[0075] As a gestalt of the magnetic particle used for the core material of the carrier in this invention, the magnetic powder distribution carrier which consists of the ferrite particle of various configurations and the mixture of various resin and magnetic powder can be used.

[0076] Although the carrier of this invention obtained in this way can be mixed with a well-known toner and it can also be used as a magnetic brush developer for electrophotography When the toner to apply is \*\*\*\*\* (ed) outside in the compound which consists of a metal which has the weighted mean particle size of 3-9 micrometers, and can constitute an anionic polymerization catalyst as an external additive in order to improve the fluidity of a toner, or an electrification property, Wear or peeling of the enveloping layer on the front face of a carrier were not seen, but the developer (especially this invention 4) of this invention which consists of these carriers and toners became clear [ that the durable property which gives a high definition image over a long period of time and which was very excellent is shown ]. the anionic polymerization catalyst whose cut part is an external additive constituent when wear and peeling of an enveloping layer occur with an external additive at the time of durability, although it is not clear about this reason -- public funds -- it thinks because it is immediately restored by the group.

[0077] As a metal which can constitute this anionic polymerization catalyst, that whose atomic radius is too small is not desirable. When an atomic radius is small, the interaction of a metal and covering resin becomes large, and this is considered for wear and peeling of the enveloping layer at the time of durability to get worse by promoting the cleavage reaction which is the reverse reaction of a polymerization reaction.

[0078] As a standard of the desirable atomic radius of the metal contained in this external additive, when referred to the data of the bond distance between atoms in chemistry handbook (edited by Chemical Society of Japan) basic volume II-714 pages and Table 15-21, it turned out that a result with what [ desirable ] has the value of 1.7Å or more as the bond distance with the oxygen at the time of forming a metallic oxide is given.

[0079] Moreover, it is desirable that it is the metallic oxide whose front face is the mean particle diameter of 0.005-0.2 micrometers by which hydrophobing processing was carried out as a compound which consists of a metal which can constitute the anionic polymerization catalyst \*\* (ed) by the toner outside. Since the electrification property under highly humid improves in addition to condensation of a primary particle being prevented by hydrophobing processing, when it \*\*\*\*\* a toner and outside, the toner which has a fluid and good high electrification property is obtained. Here, a result with 40 - 75% desirable as whenever [ hydrophobing / of a metallic oxide ] is given. At less than 40%, the amount of electrifications under highly humid falls, and it will become lacking in endurance, and the rise of the amount of electrifications becomes easy to generate under damp what carried out hydrophobing processing at the time of durability while the restoration effectiveness of covering resin falls and

endurance falls, since the interaction between a metallic oxide and carrier covering resin is barred, until it exceeds 75%.

[0080] Moreover, when the mean particle diameter of a metallic oxide is larger than 0.2 micrometers, fluid grant ability is low, and it becomes that it is easy to be embedded at a toner at the time of durability when it is less than 0.005 micrometers, and the endurance as a developer will fall.

[0081] Furthermore, in order to raise a restoration operation of the carrier covering resin by such metallic oxides, it is also important to use what has large surface area. If the thing more than 90m<sup>2</sup>/g is used as a BET specific surface area of a metallic oxide, specifically, a very desirable result will be obtained. Moreover, the addition to a toner is also important and it is good to use the addition so that it may be set to  $A \times B = 50-300$  when the BET specific surface area of A % of the weight and a metallic oxide is set to Bm<sup>2</sup>/g to a toner. When exceeding 300, in order less than 50 are insufficient as for a restoration operation of covering resin, and to see reverse \*\*\*\* of a restoration reaction, covering resin can be shaved and it becomes easy to generate \*\*\*\*\* conversely.

[0082] As a concrete compound of these metallic oxides, the alumina or titanium oxide by which hydrophobing processing was carried out is preferably used in respect of both fluid grant ability and an electrification property. In addition, in a restoration operation of covering resin, the crystal structure of a metallic oxide is also important, and especially gamma-alumina or amorphous mold titanium oxide has the high restoration operation effectiveness. These compounds are independent, or are used together, or it can mix with other external additives and they can be used.

[0083] Furthermore, it is also an indispensable technique to use a toner with a weighted mean particle size of 3-9 micrometers as a toner concerning this invention. Thereby, a high definition image can be obtained to stability for a long period of time. As this reason, in addition to an image with it being obtained, since the toner of very small particle size has narrow particle-size-distribution width of face, it is possible [ it ] by electrifying each toner particle with a fine particle size in homogeneity with the carrier of this invention that alternative development cannot take place easily. [ there is little generating of a poor electrification toner and high definition ] If the toner which contains the particle of particle size with a particle size of 4.00 micrometers or less several 10-70% is used in that case, alternative development nature will be controlled further and will become possible [ obtaining a still higher definition image over a long period of time ]. In order to be high definition as a toner particle with a particle size of 4.00 micrometers or less is less than several 10%, there are few minute toner particles which are indispensable components, a toner particle component required for high-definition reappearance decreases by long-term use, the balance of the particle size distribution of a toner collapses, and the inclination for image quality to deteriorate is shown. On the other hand, if it exceeds several 70%, since it will be easy to produce the state of aggregation between toner particles and will be easy to become a toner lump, become the rough image quality, definition is reduced, or the concentration difference of the edge section of a latent image and the interior becomes large, and it is easy to become an image liable to an inside omission.

[0084] In addition, generally, although it is necessary to increase the quantity of additions, such as a flow improver, \*\*\*\* of the carrier surface coating resin by such additive pulverized coal tends to get worse as a result, and it is easy to cause the fall of endurance as the particle size of a toner becomes fine.

[0085] However, the fall of endurance will be sharply reduced like this invention by using it combining the toner containing the carrier and the specific external additive which have a specific surface configuration.

[0086] Furthermore, it is more desirable to use the toner which has the value of 1 - 30 KOHmg/g as the acid number. If an electrification rate tends to fall, the durable property under damp also falls and the acid number exceeds 30 KOHmg/g when the acid number uses the toner of less than 1 KOHmg/g, it becomes easy to reveal the charge on the front face of a toner, and an electrification property will fall with durability.

[0087] Moreover, it is much more desirable to use the toner which is in the range whose glass transition temperature is 45-70 degrees C, and is in the range whose temperature which shows the apparent

viscosity of 105 morepoise is 80-120 degrees C. When the temperature which shows the apparent viscosity whose glass transition temperature is less than 45 degrees C or 105poise is less than 80 degrees C, it is easy to generate carrier SUPENTO at the time of long-term use of a developer, and when glass transition temperature is higher than 70 degrees C or the temperature which shows the apparent viscosity of 105poise is higher than 120 degrees C, it becomes difficult to maintain fixable [ of the toner to a toner imprint object top ], with the endurance of a developer maintained.

[0088] Although there is especially no limit as binding resin for toners, it is desirable to contain C and the polar group which consists of atoms other than H. It is because the compatibility of a polyolefin resin and a toner with a low polarity falls by this and carrier SUPENTO by the toner is controlled further. Good endurance will be acquired if a macromolecule with the value of or more  $17.0(\text{J}/\text{cm}^3)^{1/2}$  solubility parameters is used as binding resin for toners as a concrete index.

[0089] Here, the solubility parameter of a polymer can be estimated in the following procedures. The polymer measured to a series of different solvents and mixed solvents of the value of a solubility parameter little by little is added, and let the solubility parameter of the solvent untied best be the solubility parameter of a polymer. The polymer which is hard to dissolve makes the solubility parameter of the solvent with which the amount of swelling serves as max the solubility parameter of a polymer.

[0090] Moreover, a result also with more desirable also adding and using wax-like matter, such as polyethylene or polypropylene, into the toner concerning this invention is given. Although such additives are generally used in order to improve the mold-release characteristic at the time of hot calender roll fixing, in this invention, the endurance of a developer will improve further. Although the reason is unknown, it thinks because such wax-like matter can delete the coat material in a carrier front face and is used for restoration of the section or the peeling section. As an addition of this wax-like matter, 0.1 - 20.0 % of the weight is desirable. At less than 0.1 % of the weight, when improvement in the endurance of the carrier by restoration operation is not found but it exceeds 20.0 % of the weight, the compatibility of a toner and a carrier improves, and since carrier SUPENTO by the toner gets worse, the endurance of a carrier is in the inclination to fall conversely.

[0091] When mixing the carrier and toner concerning this invention and preparing the two component developer concerning this invention, if 2.0 - 15 % of the weight carries out the mixed ratio to 3.0 - 14% of the weight desirable still more preferably as toner concentration in a developer, a very good result will be obtained. At less than 2.0 % of the weight, in addition to image concentration being low, it becomes it is remarkable and impossible to use degradation of the image quality at the time of durability, and in the case where it exceeds 15 % of the weight, toner concentration makes fogging and scattering inside the plane increase, and serves as shorter \*\*\*\*\* in the useful life longevity of a developer.

[0092] Next, the image formation approach of this invention 5 using the above-mentioned binary system developer is explained.

[0093] The image formation approach of this invention carries out circulation conveyance of the binary system developer which has a toner and a carrier on developer support, and develops the latent image currently held at the latent-image supporter in the development field of a latent-image supporter and the development support which counters it with the toner of the binary system developer on this developer support.

[0094] The magnetic properties of a carrier are influenced by the magnet roller built in the development sleeve, and affect the development property and conveyance nature of a developer greatly.

[0095] In the image formation approach of this invention, the electrostatic latent image which fixed the magnet roller among the magnet rollers built in a development sleeve (developer support) and this, rotated the development sleeve alone, carried out circulation conveyance of the binary system developer which consists of a carrier which consists of a magnetic particle, and an insulating color toner on the development sleeve, and was held on the electrostatic latent-image supporter front face with this binary system developer is developed.

[0096] Especially in the image formation approach of this invention, it considers as 5 pole configurations whose \*\* this magnet roller has a repulsion pole, and the flux density in \*\* development

field is 500-1200 gauss, and when the saturation magnetization of \*\* carrier is 20-70Am<sup>2</sup>/kg, in a color copy, it excels and is suitable for the homogeneity of an image, or a tone reproduction.

[0097] In the image formation approach of this invention, it is desirable to impress development bias in a development field and to develop an electrostatic latent image with the toner of a binary system developer.

[0098] The image formation equipment which can enforce the image formation approach of this invention is explained using drawing 3.

[0099] In drawing 3, image formation equipment has the photoconductor drum 1 as an electrostatic latent-image supporter, with the developer 4, it is divided by the septum 67 at a processing laboratory (the 1st room) R1 and the churning room (the 2nd room) R2, as for the interior of the development container 66, a septum 67 is separated above the churning room R2, and the toner stockroom R3 is formed. The developer 69 is held in the processing laboratory R1 and the churning room R2, and the toner 68 for supply (nonmagnetic toner) is held in the toner stockroom R3. In addition, an opening 70 is established in the toner stockroom R3, and fall supply of the toner 68 for supply of the amount corresponding to the toner consumed through the opening 70 is carried out into the churning room R2.

[0100] The conveyance screw 63 is formed in the processing laboratory R1, and the developer 69 in a processing laboratory R1 is conveyed by the rotation drive of this conveyance screw 63 towards the longitudinal direction of the development sleeve 61. Similarly, the conveyance screw 64 is formed in a stockroom R2, and the toner which fell in the churning room R2 from the opening 70 is conveyed along with the longitudinal direction of the development sleeve 61 by rotation of the conveyance screw 64.

[0101] A developer 69 is a binary system developer with a nonmagnetic toner and a magnetic carrier.

[0102] Opening is prepared in the part close to the photoconductor drum 1 of the development container 66, and the development sleeve 61 is formed outside for the gap between the projection, the development sleeve 61, and the photoconductor drum 1 from this opening. The bias impression means 80 for impressing bias to the development sleeve 61 formed in nonmagnetic material is arranged.

[0103] As mentioned above, the magnet roller 62 as a field generating means fixed in the development sleeve 61, i.e., a magnet, has the development magnetic pole S2, the magnetic pole N2 located in the lower stream of a river, and the magnetic poles N3, S1, and N1 for conveying a developer 69. The magnet 62 is arranged in the development sleeve 61 so that the development magnetic pole S2 may counter a photoconductor drum 1. The development magnetic pole S2 forms a field near the development section between the development sleeve 61 and a photoconductor drum 1, and a magnetic brush is formed of this field.

[0104] 300-2000 micrometers of the edge of the nonmagnetic blade 65 where the regulation blade 65 which is arranged above the development sleeve 61 and regulates the thickness of the developer 69 on the development sleeve 61 is produced by aluminum and the non-magnetic material like SUS316, and page [ of a development sleeve / 61st ] distance are 400-1500 micrometers preferably. If this distance is smaller than 300 micrometers, while a magnetic carrier will be got blocked in the meantime and will tend to produce nonuniformity in a developer layer, a developer required to perform good development cannot be applied, but there is a trouble that only a development image with much nonuniformity with thin concentration is obtained. In order to prevent ununiformity spreading (the so-called blade \*\*\*\*\*) by the unnecessary particle intermingled in a developer, 400 micrometers or more are desirable. If larger than 1000 micrometers, while the amount of developers applied to up to the development sleeve 61 will increase, and predetermined developer thickness cannot be regulated but adhesion of the magnetic carrier particle to a photoconductor drum 1 will increase, circulation of a developer and the development regulation with the nonmagnetic blade 65 become weaker, TORIBO of a toner runs short and there is a trouble of fogging-coming to be easy.

[0105] -5 degrees - 35 degrees of include angles theta 1 are 0 degree - 25 degrees preferably. In the case of theta1<-5 degree, the developer thin layer formed of the magnetic force committed to a developer, the reflection force, cohesive force, etc. is sparse, and it is difficult to become what has many nonuniformity, and for developer coverage to increase with a nonmagnetic blade in the case of theta> 35 degrees, and to obtain the predetermined amount of developers.

[0106] A motion becomes late as this magnetic carrier particle layer separates from a sleeve front face by keeping with the restraint based on magnetic force and gravity, and the conveyance force to the migration direction of a sleeve 61, even if the rotation drive of the sleeve 61 is carried out in the direction of an arrow head. There are some which fall under the effect of gravity, of course.

[0107] Therefore, it conveys in the magnetic pole N1 direction, and the moving bed is formed, so that a magnetic carrier particle layer is close to a sleeve by choosing suitably the arrangement location of magnetic poles N1 and N2, the fluidity of a magnetic carrier particle, and magnetic properties. A developer is conveyed with rotation of the development sleeve 61 to a development field by migration of this magnetic carrier particle, and development is presented. 71 is the upstream toner scattering control section, and 72 is the downstream toner scattering control section, and is suppressing generating of toner scattering by this upstream toner scattering control section 71 and the downstream toner scattering control section 72. Below, the measuring method in this invention is described.

[0108] (1) By equipping the laser diffraction type particle-size-distribution measuring device HELOS (JEOL Co., Ltd. make) with dry type distribution equipment RODOS (JEOL Co., Ltd. make), and dividing the 32 logarithms of the range of 0.05 micrometers - 200 micrometers, the measuring device of the particle size distribution of a carrier was measured 3 times under the conditions of dispersive pressure 300kPa, took the average, and made it the volume particle size distribution of a carrier. The carrier particle-size list which starts this invention from there was asked for the content of a particle with a particle size of 27.5 micrometers or less. In addition, particle size in this invention was made into the median size (50% mean particle diameter).

[0109] (2) The BHU-60 mold magnetization measuring device (product made from the Riken measurement) was used for the measuring device of the magnetic properties of a carrier. About 1.0g weighing capacity of the test portion is carried out, and it is set to bore 7mmphi and a cel with a height of 10mm at a click and above equipment. Measurement adds an impression magnetic field gradually and is changed up to a maximum of 238.8 kA/m (3000 oersteds). Subsequently, impression magnetic fields are made to decrease in number, and, finally the hysteresis curve of a sample is obtained in the record paper. From this, saturation magnetization, residual magnetization, and coercive force are searched for.

[0110] (3) Measurement of the resistance of the measuring method carrier particle of the electric resistance of a carrier particle was measured using the cel shown in drawing 1. That is, Cel A was filled up with the carrier particle, electrodes 11 and 12 have been arranged so that this restoration carrier particle may be touched, the direct current voltage of 0.5-1kV was impressed to this inter-electrode one, and it asked by measuring the current which flows then. The Measuring condition is 15kg of loads of 2 and thickness of  $d = 3\text{mm}$  with a touch area [ with the cel of a restoration carrier particle ] of  $S = 2\text{cm}$ , and an up electrode. In addition, for ampere meter and 15, as for a voltage stabilizer and 17, a voltmeter and 16 are [ 13 / an insulator and 14 / a carrier particle and 18 ] guide rings.

[0111] (4) Although the mean particle diameter and particle size distribution of a measurement toner of a toner are measurable using a Coulter counter TA-II mold or a coal tar multi-sizer (coal tar company make), connect interface (product made from department machine of day), and PC9801 personal computer (NEC make) which outputs number distribution and a volume integral cloth using a coal tar multi-sizer (coal tar company make) in this invention, and the electrolytic solution prepares a NaCl water solution 1% using the 1st class sodium chloride. [ of particle size distribution (weighted mean particle size) ] For example, ISOTON R-II (made in coal tar scientific Japan) can be used. as a measuring method -- the inside of 100-150ml of said electrolysis water solutions -- as a dispersant -- a surface active agent -- 0.1-5ml of alkylbenzene sulfonate is added preferably, and 2-20mg of test portions is added further. It computed a volume integral cloth and number distribution by the electrolytic solution which suspended the sample having performed distributed processing for about 1 - 3 minutes with the ultrasonic distribution vessel, and having measured the volume of a toner 2 micrometers or more, and the number for every channel by said coal tar multi-sizer, using 100-micrometer aperture as an aperture. And it asked for the weighted mean particle size (D4) of the volume criteria searched for from number% of pieces of the particle with a particle size [ of the place concerning this invention ] of 4.00 micrometers or less, and the volume integral cloth.

[0112] (5) The scanning electron microscope was used for the number mean particle diameter on the measurement toner particle of the number mean particle diameter of an external additive (metallic compounds), it observed it by 50,000 times, carried out the quality of the 100 particles in a visual field in the X-ray microanalyser (XMA), measured the particle diameter, and asked for number mean particle diameter.

[0113] (6) Carry out weighing capacity of the acid-number measuring method samples 2-10g to a 200-300ml Erlenmeyer flask, and, in addition, dissolve resin about 50ml of mixed solvents of methanol:toluene=30:70. As long as it seems that solubility is bad, a small amount of acetone may be added. It titrates with N / 10 alkalinity potassium-hydroxide alcoholic solution by which standardization was beforehand carried out to 0.1% of bromthymol blue using the mixed indicator of Phenol Red, and the acid number is calculated by the next count from the consumption.

[0114]

Acid number = KOH solution consumption (ml) xNx56.1-/sample weight (g)

(However, N N/10 factor of KOH)

[0115] (7) Measure in measurement this invention of glass transition temperature Tg using a differential-thermal-analysis measuring device (DSC measuring device) and DSC-7 (PerkinElmer, Inc. make). A test portion carries out weighing capacity of the 5-20mg 10mg to a precision preferably. This is put in into an aluminum pan and it measures under ordinary temperature normal relative humidity by the programming rate of 10 degrees C / min between 30-200 degrees C of measurement temperature requirements, using an empty aluminum pan as a reference. In this temperature up process, the endoergic peak of the Maine peak in the range of 40-100-degree C temperature is acquired. Let the intersection of the line of the midpoint of the base line, and a differential heat curve be the glass transition temperature Tg in this invention after coming out before the endoergic peak at this time comes out.

[0116] (8) Use measurement flow tester CFT-500 mold (Shimadzu make) of toner viscosity. A sample carries out about 1.0g weighing capacity of the 60-mesh pass article. A molding machine is used and this is pressurized for 1 minute by the 100kg/cm2 load. On condition that the following, flow tester measurement is performed for this pressurization sample under (temperature of about 20-30 degrees C, 30 - 70% of humidity (RH)) ordinary temperature normal relative humidity, and an apparent-viscosity abbreviation vs. temperature curve is obtained. From the obtained smooth curve, temperature when the viscosity whose sample is 105poise is shown is searched for.

[0117]

RATE TEMP 6.0 D/M (a part for degree-C/)

SET TEMP 50.0 DEG (degree C)

MAX TEMP 180.0 DEG (degree C)

INTERVAL 3.0 DEG PREHEAT 300.0 SEC (second)

LOAD 20.0 KGF (kg)

DIE(DIA) 1.0 MM (mm)

DIE(LENG) 1.0 MM (mm)

PLUNGER 1.0 CM2 (cm2)

[0118] (9) Amount measurement drawing 2 of electrifications is the explanatory view of the equipment which measures the amount of electrifications of a toner. First, about 0.5-1.0g (developer) of mixture of the toner which is going to measure the amount of frictional electrifications, and a carrier is put into the metal measurement container 22 which has the screen 23 of 500 meshes in a bottom, and it is covered with the metal cover 24. Weight of the measurement container 22 whole at this time is made into \*\*\*\* W1 (kg). Next, in the suction machine 21 (the part which touches the measurement container 22 is an insulator at least), it draws in from the suction opening 27, the airflow control valve 26 is adjusted, and the pressure of a vacuum gage 25 is set to 2450Pa (250mmAq). In this condition, suction is performed for about 2 minutes sufficiently preferably, and suction removal of the toner is carried out. Potential of the electrometer 29 at this time is set to V (volt). 28 is a capacitor and sets capacity to C (mF) here. Moreover, weight of the whole measurement container after suction is made into \*\*\*\* W2 (kg). The

amount (mC/kg) of frictional electrifications of the toner at this time is calculated like the following formula.

[0119] Amount (mC/kg) of frictional electrifications =  $(CxV)/\text{of a toner } (W1-W2)$

[0120] (10) Evaluation of fogging density measurement fogging is REFLECTOMETER by Tokyo Denshoku Co., Ltd. It measured with the Green filter using MODELTC-6DS, and computed from the following formula. There is so little fogging that a numeric value is small.

[0121]

[Equation 1]

カブリ (反射率) (%) = 標準紙の反射率 (%) - サンプルの非画像部の反射率 (%)

[0122] (11) Whenever [ hydrophobing / which is specified in a measurement book specification whenever / hydrophobing ] is measured by the methanol titration trial shown below. 0.2g of compounds for outside \*\* is added in 500ml of water in a container. A methanol is measured until humidity of the whole quantity of the compound for outside \*\* is carried out from view let. Under the present circumstances, the solution in a container is always agitated with a magnetic stirrer. The terminal point is observed when the whole quantity of the compound for outside \*\* suspends in a liquid, and whenever [ hydrophobing ] is expressed as weight [ of the methanol at the time of arriving at a terminal point, and the methanol in the liquefied mixture of water ] %.

[0123] (12) The measurement BET specific surface area of a BET specific surface area uses the Yuasa Ionics make, the amount measuring device of full automatic gas adsorption, and auto SOBU 1, uses nitrogen for adsorption gas, and asks for it by the BET multipoint method. In addition, as pretreatment of a sample, degassing of 10 hours is performed at 50 degrees C.

[0124] (13) Measurement of the measurement molecular weight of the molecular weight of polyolefin resin used the Waters gel-permeation-chromatography (GPC) measuring device and GPC-150C, and measured them on condition that the following.

Column: GMH-HT30cm Two reams (TOSOH [ CORP. ] CORP. make)

Temperature: 145 degrees C Solvent: o-dichlorobenzene (0.1% ionol addition)

The rate of flow: 1.0 ml/min Sample: Use the obtained solid content as a sample after performing a Soxhlet extraction for 20 hours using a toluene solvent in the case of the determination of molecular weight of 0.4ml impregnation carrier covering resin, removing toluene from an extract by an evaporator etc. and drying 0.15% of sample. The molecular-weight calibration curve created by the mono dispersion polystyrene standard sample in molecular-weight calculation of a sample is used, and it is computed.

[0125]

[Example] Although the example of this invention is shown below, this invention is not limited to these at all. The "section" means the "weight section."

[0126] Put in and carried out the temperature up of purification n-heptane 100ml, 10g of magnesium stearates, and the 0.33g of the titanium tetrachlorides to the 500ml flask which carried out the example of the <this invention 1> carrier manufacture 1 argon permutation, it was made to react under a ring current for 2 hours, and the titanium content catalyst component was obtained. The temperature up of 600g of Cu-Zn system ferrite impalpable powder with a particle size of 35 micrometers and 0.6g (an equivalent for 0.1 millimol) of titanium content catalyst components which carried out dehydration desiccation was put in and carried out to the 3000ml flask prepared independently at 150 degrees C under purification n-heptane 1000ml and reduced pressure, heat-treatment was performed for bottom 1 hour of a ring current, and mixture (1) was obtained. Next, mixture (1) is put in into an autoclave with a volume of 3000ml which carried out the argon permutation. After adding a purification n-heptane and setting the whole quantity to 1500ml, triethylaluminum 10 millimols, Ten millimols of diethyl aluminum mono-chloride are added. At 80 degrees C After a temperature up, A polymerization reaction is performed for 30 minutes, supplying [ supply hydrogen to 392kPa(s) (4kg/cm2G), and ] ethylene and a propylene continuously by 9/1 of volume ratios so that total pressure may be maintained at 882kPa(s) (9kg/cm2G). The polyolefin resin covering carrier (1) with the physical-properties value shown in Table

1 was obtained.

[0127] Various 4 and 6 - 7 polymerization monomer presentations and carrier core materials were changed, and the example 2 of carrier manufacture - polyolefin resin covering carrier [ with the physical-properties value shown in Table 1 by the same approach as the example 1 of carrier manufacture ] (2) - (4), (6), and (7) were obtained.

[0128] be alike Spira Cota (Okada elaborate company make) to the ferrite impalpable powder 100 section used in the example 1 of carrier manufacture using the xylene solution (0.5 % of the weight of polyethylene resin solid content) 400 section of example of carrier manufacture 5 low-density-polyethylene resin / polypropylene resin =9/1 -- RIPORI ethylene resin was applied and the polyolefin resin covering carrier (5) with the physical-properties value shown in Table 1 was obtained.

[0129]

[Table 1]

キャリア製造例 (キャリアNo.)	モノマー組成	粒径 ( $\mu\text{m}$ )	電気抵抗 ( $\Omega \cdot \text{cm}$ )		飽和磁化 (79.6kA/m)	被覆方法
			(0.5kV)	(1kV)		
1	エチレン/プロピレン (9/1)	35	$10^8$	$10^8$	$61\text{Am}^2/\text{kg}$	表面重合法
2	エチレン/プロピレン (1/9)	35	$8 \times 10^8$	$7 \times 10^7$	$61\text{Am}^2/\text{kg}$	表面重合法
3	エチレン/ブタジエン (9/1)	35	$7 \times 10^8$	$3 \times 10^7$	$61\text{Am}^2/\text{kg}$	表面重合法
4	エチレン/プロピレン (9/1)	66	$10^8$	$9 \times 10^7$	$61\text{Am}^2/\text{kg}$	表面重合法
5	エチレン/プロピレン (9/1)	39	$10^8$	$4 \times 10^7$	$61\text{Am}^2/\text{kg}$	湿式コート
6	エチレンのみ	35	$3 \times 10^{10}$	$10^8$	$61\text{Am}^2/\text{kg}$	表面重合法
7	プロピレンのみ	35	$8 \times 10^8$	$6 \times 10^7$	$61\text{Am}^2/\text{kg}$	表面重合法

[0130]

Example 1 of black fine-particles manufacture - propoxy-ized bisphenol / ethoxylation bisphenol (mole ratio 1:1)

A fumaric acid/trimellitic acid (mole ratio 19:1)

The polyester resin obtained by condensing The 100 sections - carbon black The four sections The chromium compound of a - G tert-butyl salicylic acid The Henschel mixer performed preliminary mixing enough, melting kneading was carried out with the 2 shaft extrusion type kneading machine, and coarse grinding of the 4 section was carried out to about 1mm using the hammer mill after cooling, and, subsequently it was pulverized with the pulverizer by the air jet method. Furthermore, pneumatic elutriation of the obtained pulverizing object was carried out, and the black fine particles (1) whose weighted mean particle size is 7 micrometers were obtained.

[0131] The example of toner manufacture 1 black fine-particles (1) 100 section and the titanium oxide impalpable powder (mean particle diameter of 0.05 micrometers) 1.5 section which carried out hydrophobing processing of the front face were mixed with the Henschel mixer, and the toner (1) was obtained.

[0132] The example of toner manufacture 2 black fine-particles (1) 100 section and the alumina impalpable powder (mean particle diameter of 0.04 micrometers) 1.5 section which carried out hydrophobing processing of the front face were mixed with the Henschel mixer, and the toner (2) was obtained.

[0133] The value of 114 degrees C in the temperature which shows the apparent viscosity of acid-number 13 KOHmg/m,  $T_g=64$  degree C, and 105poise as the above-mentioned toner (1) and a physical-properties value of (2) was acquired by the analytical method which carried out point \*\*.

[0134] The carrier (1) was mixed with example 1 toner (1) at 3% of toner concentration, the developer was produced, and \*\*\*\*\*-proof was performed using color copying machine CLC-500 (Canon make) converted so that the rotational speed of developer support (sleeve) might become 2.5 times by the peripheral-speed ratio to the rotational speed of a photo conductor as image formation equipment shown in drawing 3. First, after performing empty rotation for the development counter containing a developer under 25 degrees C / 10% of environment for 2 hours, the development counter was returned to the body of a copying machine, and 5000-sheet \*\*\*\*\* was performed using the original manuscript of 30% of rates of image surface ratio. Next, after performing empty rotation again for 2 hours, 5000-sheet \*\*\*\*\* was again performed using the original manuscript of 30% of rates of image surface ratio. Together with the following examples of an experiment, a result is shown in Table 2. As shown in Table 2, in degradation and \*\*\*\*\*-proof according [ an above-mentioned developer ] to empty rotation, there were little amount change of electrifications and degradation of an image property, and the result which shows the very good endurance as which neither SUPENTO nor toner scattering is also regarded was obtained.

[0135] Except changing example 2 toner (1) into a toner (2), when the same experiment as an example 1 was conducted, the result which shows very good endurance as shown in Table 2 was obtained.

[0136] The good result was obtained, as it was the level in which all do not have a problem practically although fogging got worse slightly in the second half of a durability test when the experiment same except making example 3 toner concentration into 14% as an example 1 was conducted, and toner scattering was slightly seen to the after [ durability ] inside of a plane and another durable property was also shown in Table 2.

[0137] Except changing example 4 carrier (1) into a carrier (2), when the same experiment as an example 1 was conducted, the result which shows a good durable property as shown in Table 2 was obtained.

[0138] Except changing example 5 carrier (1) into a carrier (3), when the same experiment as an example 1 was conducted, the result which shows very good endurance as shown in Table 2 was obtained.

[0139] Except changing example of reference 1 carrier (1) into a carrier (7), when the same experiment as an example 1 was conducted, the amount of electrifications became lowness a little, and toner scattering was slightly looked at by the after [ durability ] inside of a plane. Since carrier particle size was large, carrier surface area was small and it thought because the electrification rate is not quick, but it was the level which is satisfactory practically, and it was good as other durable properties were also shown in Table 2.

[0140]

[Table 2]

	キャリア (No.)	トナー (No.)	トナー 濃度 (%)	帯電量 (-nC/kg)					マクベス画像濃度					カブリ濃度 (%)					トナー 飛散 (耐久後) (SEM観察)	シート
				初期	空回転 2時間後	面出し 5分後	空回転 2時間後	面出し 5分後	初期	空回転 2時間後	面出し 5分後	空回転 2時間後	面出し 5分後	初期	空回転 2時間後	面出し 5分後	空回転 2時間後	面出し 5分後		
実施例1	1	1	3	34	36	33	36	32	1.51	1.49	1.50	1.48	1.49	0.1	0.2	0.3	0.3	0.4	○	○
実施例2	1	2	3	35	36	36	37	34	1.50	1.48	1.50	1.47	1.48	0.1	0.1	0.2	0.3	0.4	○	○
実施例3	1	1	14	29	30	26	30	26	1.56	1.52	1.59	1.54	1.58	0.8	0.9	1.0	0.9	1.1	△	○
実施例4	3	1	3	31	33	29	32	29	1.57	1.55	1.56	1.54	1.55	0.2	0.4	0.4	0.4	0.5	○	○
実施例5	6	1	3	35	37	36	38	34	1.60	1.49	1.49	1.45	1.48	0.1	0.3	0.3	0.3	0.5	○	○
参考例1	7	1	3	30	32	26	31	25	1.58	1.54	1.63	1.60	1.68	0.3	0.5	0.8	0.9	1.0	△	○

表中、○：非常に良好  
△：実用上問題無し

[0141] Except changing example 6 carrier (1) into a carrier (5), when the same experiment as an example 1 was conducted, toner scattering was slightly looked at by the after [ durability ] inside of a plane, and carrier SUPENTO was slightly looked at in SEM observation of the carrier after durability. Although the surface covering condition was considered that are uneven, and carrier SUPENTO occurred and grew up to be a non-coat part since the covering approach of polyolefin resin was a wet method, it was the level in which all do not have a between title practically.

[0142] Except changing example of reference 2 carrier (1) into a carrier (6), when the same experiment as an example 1 was conducted, the amount of electrifications became lowness a little, and toner

scattering was looked at by the after [ durability ] inside of a plane. Although it thought because electrification grant ability is not enough by the resin presentation consisting of only ethylene monomers, it was the level which is satisfactory practically.

[0143] Except changing example of reference 3 carrier (1) into a carrier (7), when the same experiment as an example 1 was conducted, in SEM observation of the carrier after durability, carrier SUPENTO was seen slightly. Although it thought because SUPENTO-proof nature is not enough by the resin presentation consisting of only propylene monomers, it was the level which is satisfactory practically.

[0144] Put in and carried out the temperature up of purification n-heptane 100ml, 10g of magnesium stearates, and the 0.33g of the titanium tetrachlorides to the 500ml flask which carried out the example of the <this invention 2> carrier manufacture 8 argon permutation, it was made to react under a ring current for 2 hours, and the titanium content catalyst component was obtained. The temperature up of 600g of ferrite impalpable powder of the contents and 0.6g (an equivalent for 0.1 millimol) of titanium content catalyst components shown in Table 3 which carried out dehydration desiccation was put in and carried out to the 3000ml flask prepared independently at 150 degrees C under purification n-heptane 1000ml and reduced pressure, heat-treatment was performed for bottom 1 hour of a ring current, and mixture (8) was obtained. Next, mixture (8) is put in into an autoclave with a volume of 3000ml which carried out the argon permutation. After adding a purification n-heptane and setting the whole quantity to 1500ml, triethylaluminum 10 millimols, Ten millimols of diethyl aluminum mono-chloride are added. At 80 degrees C After a temperature up, The polymerization reaction was performed for 30 minutes, supplying [ supplied hydrogen to 392kPa(s) (4kg/cm2G), and ] ethylene gas continuously so that total pressure may be maintained at 882kPa(s) (9kg/cm2G), and the polyolefin resin covering carrier (8) was obtained.

[0145] The thing of the contents shown in Table 3 as the example 9 of carrier manufacture - a 12 carrier core material was used, and the polyolefin resin covering carriers 9-12 were obtained by the same approach as the example 8 of carrier manufacture.

[0146]

[Table 3]

キャリア製造例 (キャリアNo.)	フェライト成分の組成 (モル%)			メジアン径 ( $\mu$ m)	電気抵抗 ( $\Omega \cdot \text{cm}$ )		飽和磁化 ( $\text{Am}^2/\text{kg}$ )
	$\text{Fe}_2\text{O}_3$	MnO	添加物		(0.5kV)	(1kV)	
8	60	28	$\text{CaO}$ , 12	40	$9 \times 10^4$	$6 \times 10^4$	61
9	60	28	$\text{CaO}$ , 12	70	$9 \times 10^4$	$6 \times 10^4$	61
10	60	34	$\text{SrO}$ , 6	40	$5 \times 10^4$	$9 \times 10^4$	62
11	60	30	$\text{Na}_2\text{O}$ , 10	40	$2 \times 10^4$	$3 \times 10^4$	60
12	60	24	$\text{K}_2\text{O}$ , 16	40	$10^4$	$3 \times 10^4$	58

[0147] Example 2 of black fine-particles manufacture - propoxy-ized bisphenol / ethoxylation bisphenol (mole ratio 1:1)

A fumaric acid/trimellitic acid (mole ratio 19:1)

The polyester resin obtained by condensing The 100 sections - carbon black The five sections The chromium compound of a - G tert-butyl salicylic acid The Henschel mixer performed preliminary mixing enough, melting kneading was carried out with the 2 shaft extrusion type kneading machine, and coarse grinding of the 3 section was carried out to about 1mm using the hammer mill after cooling, and, subsequently it was pulverized with the pulverizer by the air jet method. Pneumatic elutriation of the pulverizing object furthermore obtained was carried out, and the black fine particles (2) whose weighted mean particle size is 7 micrometers were obtained.

[0148] The example of toner manufacture 3 black fine-particles (2) 100 section and the titanium oxide impalpable powder (mean particle diameter of 0.05 micrometers) 1.5 section which carried out hydrophobing processing of the front face were mixed with the Henschel mixer, and the toner (3) was obtained.

[0149] The example of toner manufacture 4 black fine-particles (2) 100 section and the alumina impalpable powder (mean particle diameter of 0.04 micrometers) 1.5 section which carried out hydrophobing processing of the front face were mixed with the Henschel mixer, and the toner (4) was obtained.

[0150] The value of 114 degrees C in the temperature which shows the apparent viscosity of acid-number 13 KOHmg/g, Tg=64 degree C, and 105poise as the above-mentioned toner (3) and a physical-properties value of (4) was acquired by the analytical method which carried out point \*\*.

[0151] The carrier (8) was mixed with example 7 toner (3) at 13% of toner concentration, the developer was produced, and \*\*\*\*\*-proof was performed using color copying machine CLC-500 (Canon make) converted so that the rotational speed of developer support (sleeve) might become 0.7 times by the peripheral-speed ratio to the rotational speed of a photo conductor as image formation equipment shown in drawing 3. First, after performing empty rotation for the development counter containing a developer under 30 degrees C / 90% of environment for 2 hours, the development counter was returned to the body of a copying machine, and 10000-sheet \*\*\*\*\* was performed using the original manuscript of 30% of rates of image surface ratio. Together with the following examples of an experiment, a result is shown in Table 4. As shown in Table 4, the above-mentioned developer had little amount change of electrifications, and degradation of an image property in degradation and \*\*\*\*\*-proof by empty rotation, by the ability maintaining good imprint nature, very good highlights section image quality was always given, and the result which shows the very good endurance as which neither SUPENTO nor toner scattering is also regarded was obtained.

[0152] When example 8 toner (3) was changed into the toner (4) and the same experiment as an example 7 was conducted, the result which shows very good imprint nature (highlights section image quality) and endurance as shown in Table 4 was obtained.

[0153] Example 9 carrier (8) was changed into the carrier (9), and when it mixed at 10% of toner concentration, the developer was produced and the same experiment as an example 7 was conducted, some toner scattering was seen by the after [ durability ] inside of a plane. Since carrier particle size was large, carrier surface area was small, although it thought since the electrification property fell, it was the level which is satisfactory practically and other properties did not have a problem, either.

[0154] When example 10 carrier (8) was changed into the carrier (10) and the same experiment as an example 7 was conducted, the result which shows very good imprint nature (highlights section image quality) and endurance as shown in Table 4 was obtained.

[0155] When an example 11 and 12 carriers (8) were changed into a carrier (11) and (12) and the same experiment as an example 7 was conducted, toner SUPENTO was slightly seen on the carrier front face after durability. Although it was considered also since alkaline earth metal did not contain in the core material component, and the adhesion or catalytic activity of a polymerization catalyst was a little inadequate, there is no problem practically and the result which is satisfactory as other durable properties are especially shown in Table 4 was obtained.

[0156]

[Table 4]

	キ+77 (No.)	ト- (No.)	ト- 濃度 (%)	帯電量(-nC/kg)			マクベス面電圧			カブリ濃度 (%)			ハイライト部面質			ト-飛散 (耐久後)	メット (SEM観察)
				初期	空回転 2時間後	熱処理後 10%後	初期	空回転 2時間後	熱処理後 10%後	初期	空回転 2時間後	熱処理後 10%後	初期	空回転 2時間後	熱処理後 10%後		
実施例7	8	3	13	35	35	34	1.64	1.62	1.64	0.3	0.4	0.5	○	○	○	○	○
実施例8	8	4	13	33	33	32	1.68	1.67	1.68	0.3	0.5	0.5	○	○	○	○	○
実施例9	9	3	10	30	28	26	1.61	1.63	1.66	0.4	0.5	0.8	○	○	△	△	○
実施例10	10	3	13	34	33	33	1.65	1.64	1.66	0.3	0.4	0.5	○	○	○	○	○
実施例11	11	3	13	32	30	28	1.71	1.71	1.78	0.4	0.5	0.9	○	○	○	○	△
実施例12	12	3	13	33	30	28	1.67	1.69	1.73	0.3	0.4	0.8	○	○	○	○	△

front Naka and O: -- very much -- fitness \*\*: -- practically -- those with problem-less x:problem (practical use is impossible)

[0157] Put in and carried out the temperature up of purification n-heptane 100ml, 10g of magnesium stearates, and the 0.33g of the titanium tetrachlorides to the 500ml flask which carried out the example of the <this invention 3> carrier manufacture 13 argon permutation, it was made to react under a ring current for 2 hours, and the titanium content catalyst component was obtained. The temperature up of 600g of ferrite impalpable powder of the contents of a presentation and 0.6g (an equivalent for 0.1 millimol) of titanium content catalyst components shown in Table 5 which carried out dehydration desiccation was put in and carried out to the 3000ml flask prepared independently at 150 degrees C under purification n-heptane 1000ml and reduced pressure, heat-treatment was performed for bottom 1 hour of a ring current, and mixture (13) was obtained. Next, mixture (13) is put in into an autoclave with a volume of 3000ml which carried out the argon permutation. After adding a purification n-heptane and setting the whole quantity to 1500ml, triethylaluminum 10 millimols, Ten millimols of diethyl aluminum mono-chloride are added. At 80 degrees C After a temperature up, The polymerization reaction was performed for 40 minutes, supplying [ supplied hydrogen to 392kPa(s) (4kg/cm<sup>2</sup>G), and ] ethylene gas continuously so that total pressure may be maintained at 882kPa(s) (9kg/cm<sup>2</sup>G), and the polyolefin resin covering carrier (13) which consists of the physical-properties value shown in Table 5 was obtained.

[0158] The thing of the contents shown in Table 5 as the example 14 of carrier manufacture - a 18 carrier core material was used, and polyolefin resin covering carrier (14) - (18) as shown in Table 5 by the same approach as the example 13 of carrier manufacture was obtained.

[0159]

[Table 5]

キャリア製造例 (キャリアNo.)	フェライト成分の組成 (重量%)			メジアン径 ( $\mu$ m)	電気抵抗 ( $\Omega \cdot \text{cm}$ )		飽和磁化 (Am <sup>2</sup> /kg)
	Fe <sub>2</sub> O <sub>3</sub>	A	B		(0.5kV)	(1kV)	
13	60	MgO (19)	MnO <sub>2</sub> (21)	40	10 <sup>9</sup>	8 × 10 <sup>9</sup>	61
14	60	MgO (19)	MnO <sub>2</sub> (21)	70	9 × 10 <sup>9</sup>	6 × 10 <sup>9</sup>	61
15	67	MgO (16)	MnO <sub>2</sub> , CaO (14, 3)	40	4 × 10 <sup>9</sup>	7 × 10 <sup>9</sup>	59
16	92	MgO (3)	SiO <sub>2</sub> (5)	40	2 × 10 <sup>11</sup>	9 × 10 <sup>10</sup>	62
17	75	MgO (19)	Al <sub>2</sub> O <sub>3</sub> (6)	40	2 × 10 <sup>9</sup>	8 × 10 <sup>9</sup>	60
18	70	MgO (0.6)	MnO <sub>2</sub> , CaO (20, 9.4)	40	3 × 10 <sup>9</sup>	5 × 10 <sup>9</sup>	64

[0160]

Examples 3 and 4 of black fine-particles manufacture - propoxy-ized bisphenol / ethoxylation bisphenol (mole ratio 1:1)

A fumaric acid/trimellitic acid (mole ratio 19:1)

The polyester resin obtained by condensing The 100 sections - carbon black The four sections The chromium compound of a - G tert-butyl salicylic acid The Henschel mixer performed preliminary mixing enough, melting kneading was carried out with the 2 shaft extrusion type kneading machine, and coarse grinding of the 3 section was carried out to about 1mm using the hammer mill after cooling, and, subsequently it was pulverized with the pulverizer by the air jet method. Furthermore, pneumatic elutriation of the obtained pulverizing object was carried out, and the black fine particles (3) whose weighted mean particle size is 7 micrometers, and the black fine particles (4) whose weighted mean particle size is 10 micrometers were obtained.

[0161] The example of toner manufacture 5 black fine-particles (3) 100 section and the titanium oxide impalpable powder (mean particle diameter of 0.05 micrometers) 3.0 section which carried out hydrophobing processing of the front face were mixed with the Henschel mixer, and the toner (5) was obtained.

[0162] The example of toner manufacture 6 black fine-particles (3) 100 section and the alumina impalpable powder (mean particle diameter of 0.04 micrometers) 3.0 section which carried out hydrophobing processing of the front face were mixed with the Henschel mixer, and the toner (6) was obtained.

[0163] The example of toner manufacture 7 black fine-particles (4) 100 section and the titanium oxide impalpable powder 3.0 section used in the example 5 of toner manufacture were mixed with the Henschel mixer, and the toner (7) was obtained.

[0164] The value of 116 degrees C in the temperature which shows the apparent viscosity of acid-number 14 KOHmg/g, Tg=63 degree C, and 105poise as a physical-properties value of above-mentioned toner (5) - (7) was acquired by the analytical method which carried out point \*\*.

[0165] Mix a carrier (13) with example 13 toner (5) at 8% of toner concentration, and a developer is produced. \*\*\*\*\*-proof depended for \*\*\*\*(ing) 10000 sheets using the original manuscript of 30% of rates of image surface ratio under 30 degrees C / 90% of temperature / humidity environment, using color copying machine CLC-500 (Canon make) as image formation equipment shown in drawing 3 was performed, and the situation of the blemish on a photo conductor was observed by viewing after the trial. Together with the result of endurance, a result is shown in Table 6 with the following examples of an experiment. As shown in Table 6, the above-mentioned developer had little amount change of electrifications, and degradation of an image property in \*\*\*\*\*-proof, and the result which shows the very good endurance as which neither SUPENTO of a carrier nor toner scattering is not only also seen, but a blemish is not regarded at all on the photo conductor after a trial was obtained.

[0166] When example 14 toner (5) was changed into the toner (6) and the same experiment as an example 13 was conducted, as shown in Table 6, the very good result was obtained.

[0167] When the carrier (13) was mixed with example 15 toner (7) at 10% of toner concentration, the developer was produced and the same experiment as an example 13 was conducted, some blemish was seen on the photo conductor after use. Although it thought since the additive which is not held on a toner front face since [ that toner particle size is large ] toner surface area is small was generated, the image top did not have a between title.

[0168] When changed example 16 carrier (13) into the carrier (14), it mixed at 6% of toner concentration, the developer was produced and the same experiment as an example 13 was conducted, some toner scattering was seen by the after [ durability ] inside of a plane, and some blemish was also seen on the photo conductor. Since carrier particle size was large, carrier surface area was small, although it thought since the electrification grant ability to an additive fell, it was the level which does not have a between title practically, and other properties did not have a between title, either.

[0169] When example 17 carrier (13) was changed into the carrier (15) and the same experiment as an example 13 was conducted, as shown in Table 6, the very good result was obtained.

[0170] When example 18 carrier (13) was changed into the carrier (16) and the same experiment as an

example 13 was conducted, some toner scattering was seen by the after [ durability ] inside of a plane, and some blemish was also seen on the photo conductor. Although it thought since resistance of a carrier was high, and the electrification rate fell, it was the level which is satisfactory practically and other properties did not have a problem, either.

[0171] When example 19 carrier (13) was changed into the carrier (17) and the same experiment as an example 13 was conducted, some toner scattering was seen by the after [ durability ] inside of a plane, and some blemish was also seen on the photo conductor. Although it thought since resistance of a carrier was low, and the electrification grant ability under highly humid fell, it was the level which is satisfactory practically and other properties did not have a problem, either.

[0172] When example 20 carrier (13) was changed into the carrier (18) and the same experiment as an example 13 was conducted, some blemish was seen on the photo conductor after durability. Although it thought since the electrification rate of an additive fell according to there being few contents of A (MgO in this case) of a ferrite constituent, it was the level which is satisfactory practically and other properties did not have a problem, either.

[0173] Except making example 21 toner concentration into 14%, when the same experiment as an example 13 was conducted, some toner scattering was seen by the after [ durability ] inside of a plane, and some blemish was also seen on the photo conductor. Although it thought since the electrification rate fell according to toner concentration being high, it was the level which does not have a between title practically, and other properties did not have a problem, either.

[0174]

[Table 6]

	キャリア (No.)	トナー (No.)	トナー 濃度 (%)	帯電量 (-nC/kg)		マパス画像濃度		おり濃度 (%)		トナー飛散 (耐久後)	スベト (SEM観察)	感光体上 の傷 (目視観察)
				初期	10k画出し後	初期	10k画出し後	初期	10k画出し後			
実施例13	13	5	8	35	34	1.64	1.65	0.3	0.4	○	○	○
実施例14	13	6	8	33	32	1.88	1.69	0.4	0.4	○	○	○
実施例15	13	7	10	30	28	1.76	1.77	0.3	0.4	○	○	△
実施例16	14	5	6	30	27	1.74	1.78	0.6	0.9	△	○	△
実施例17	15	5	8	34	33	1.65	1.66	0.3	0.4	○	○	○
実施例18	16	5	8	28	23	1.77	1.86	0.7	1.2	△	○	△
実施例19	17	5	8	26	22	1.81	1.92	0.8	1.3	△	○	△
実施例20	18	5	8	31	29	1.71	1.75	0.6	0.8	○	○	△
実施例21	13	5	14	27	22	1.80	1.98	1.1	1.7	△	○	△

front Naka and O: -- very much -- fitness \*\*: -- practically with no problem -- [0175] Put in and carried out the temperature up of purification n-heptane 100ml, 10g of magnesium stearates, and the 0.33g of the titanium tetrachlorides to the 500ml flask which carried out the example of the <this invention 4> carrier manufacture 19 argon permutation, it was made to react under a ring current for 2 hours, and the titanium content catalyst component was obtained. The temperature up of 600g of ferrite impalpable powder and 0.6g (an equivalent for 0.1 millimol) of titanium content catalyst components which carried out dehydration desiccation was put in and carried out to the 300ml flask prepared independently at 150 degrees C under purification n-heptane 1000ml and reduced pressure, heat-treatment was performed for bottom 1 hour of a ring current, and mixture (19) was obtained. Next, mixture (19) is put in into an autoclave with a volume of 3000ml which carried out the argon permutation. After adding a purification

n-heptane and setting the whole quantity to 1500ml, triethylaluminum 10 millimols, Ten millimols of diethyl aluminum mono-chloride are added. At 80 degrees C After a temperature up, A polymerization reaction is performed for 30 minutes, supplying [ supply hydrogen to 392kPa(s) (4kg/cm<sup>2</sup>G), and ] ethylene gas continuously so that total pressure may be maintained at 882kPa(s) (9kg/cm<sup>2</sup>G). A polyolefin resin covering carrier (19) with the physical-properties value shown in Table 7, and (the weight average molecular weight 360000 of covering resin and number average molecular weight 9500) were obtained.

[0176] In the example 19 of example of carrier manufacture 20 carrier manufacture, the polyolefin resin covering carrier (20) with the physical-properties value shown in Table 7 was obtained by adding carbon black 0.1g further to 600g of ferrite impalpable powder.

[0177] be alike Spira Cota (Okada elaborate company make) to the ferrite impalpable powder 100 section used in the example 19 of carrier manufacture using the xylene solution (0.5 % of the weight of polyethylene resin solid content) 400 section of example of carrier manufacture 21 low-density-polyethylene resin -- RIPORI ethylene resin was applied and a polyolefin resin covering carrier (21) with the physical-properties value shown in Table 7, and (the weight average molecular weight 35000 of covering resin and number average molecular weight 9400) were obtained.

[0178] In the example 22 of carrier manufacture - the example 19 of 26 carrier manufacture, polyethylene resin covering carrier (22) - (26) with the physical-properties value shown in Table 7 was obtained by changing various ferrite impalpable powder or polymerization conditions.

[0179]

[Table 7]

キャリア製造例 (キャリアNo.)	粒径 ( $\mu$ m)	27.5 $\mu$ m以下 (重量%)	電気抵抗 ( $\Omega \cdot \text{cm}$ )		飽和磁化 (79.6kA/m下)	被覆方法
			(0.5kV)	(1kV)		
19	38	36	$10^9$	$5 \times 10^7$	55Am <sup>2</sup> /kg	表面重合法
20	38	37	$5 \times 10^8$	$8 \times 10^8$	55Am <sup>2</sup> /kg	表面重合法
21	38	35	$10^9$	$2 \times 10^7$	55Am <sup>2</sup> /kg	湿式コート
22	70	0.8	$10^9$	$5 \times 10^7$	55Am <sup>2</sup> /kg	表面重合法
23	38	38	$2 \times 10^{11}$	$10^{10}$	55Am <sup>2</sup> /kg	表面重合法
24	38	34	$10^7$	$8 \times 10^5$	55Am <sup>2</sup> /kg	表面重合法
25	38	33	$10^9$	$6 \times 10^7$	90Am <sup>2</sup> /kg	表面重合法
26	38	36	$9 \times 10^8$	$4 \times 10^7$	10Am <sup>2</sup> /kg	表面重合法

[0180]

Example 5 of black fine-particles manufacture - propoxy-ized bisphenol / ethoxylation bisphenol (mole ratio 1:1)

A fumaric acid/trimellitic acid (mole ratio 19:1) was condensed, and it was obtained. Polyester resin (solubility parameter: 22.1(J/cm<sup>3</sup>)<sup>1/2</sup>)

Section [ 100 / ] - Polypropylene The two sections - carbon black The five sections The chromium compound of a - G tert-butyl salicylic acid The Henschel mixer performed preliminary mixing enough, melting kneading was carried out with the 2 shaft extrusion type kneading machine, and coarse grinding of the 5 section was carried out to about 1mm using the hammer mill after cooling, and, subsequently it was pulverized with the pulverizer by the air jet method. Furthermore, pneumatic elutriation of the obtained pulverizing object was carried out, and the black fine particles (5) whose weighted mean particle size is 7 micrometers were obtained.

[0181] By the same ingredient and technique as the example of black fine-particles manufacture 6 black fine-particles manufacture 5, the black fine particles (6) whose weighted mean particle size is 10 micrometers were obtained.

[0182] In the example 7 of black fine-particles manufacture - the example 5 of 10 black fine-particles manufacture, the mole ratio of a propoxy-ized bisphenol / ethoxylation bisphenol and the addition of trimellitic acid were adjusted, and black fine-particles (7) - (10) was obtained.

[0183] In the example 5 of example of black fine-particles manufacture 11 black fine-particles manufacture, black fine particles (11) were obtained by the same technique as the example 5 of black fine-particles manufacture, without using polypropylene.

[0184] By the same technique as the example 5 of black fine-particles manufacture, black fine particles (12) were obtained except changing into example of black fine-particles manufacture 12 polyester resin, and using styrene-n-butyl acrylate-methyl acrylate resin (solubility parameter:  $18.2(\text{J}/\text{cm}^3)^{1/2}$ ).

[0185] By the same technique as the example 5 of black fine-particles manufacture, black fine particles (13) were obtained except changing into example of black fine-particles manufacture 13 polyester resin, and using styrene-butadiene-rubber-isobutylene resin (solubility parameter:  $16.8(\text{J}/\text{cm}^3)^{1/2}$ ).

[0186] The weighted mean particle size of 8.6 micrometers, 8.8-micrometer black fine particles (14), and (15) were obtained by the same ingredient and technique as the example 14 of black fine-particles manufacture, and the example 1 of 15 black fine-particles manufacture.

[0187] The example of toner manufacture 8 black fine-particles (6) 100 section and the amorphous mold titanium oxide impalpable powder (whenever [ BET specific surface area  $130\text{m}^2/\text{g}$  and hydrophobing ] 71%, mean particle diameter of 0.03 micrometers) 1.5 section which carried out hydrophobing processing of the front face were mixed with the Henschel mixer, and the toner (8) of the contents shown in Table 8 was obtained.

[0188] The example of toner manufacture 9 black fine-particles (5) 100 section and the titanium oxide impalpable powder 2.5 section used in the example 8 of toner manufacture were mixed with the Henschel mixer, and the toner (9) of the contents shown in Table 8 was obtained.

[0189] The example of toner manufacture 10 black fine-particles (5) 100 section and the amorphous mold titanium oxide impalpable powder (whenever [ BET specific surface area  $91\text{m}^2/\text{g}$  and hydrophobing ] 80%, mean particle diameter of 0.04 micrometers) 1.5 section which carried out hydrophobing processing of the front face were mixed with the Henschel mixer, and the toner (10) of the contents shown in Table 8 was obtained.

[0190] The example of toner manufacture 11 black fine-particles (5) 100 section and the amorphous mold titanium oxide impalpable powder (whenever [ BET specific surface area  $87\text{m}^2/\text{g}$  and hydrophobing ] 73%, mean particle diameter of 0.04 micrometers) 1.5 section which carried out hydrophobing processing of the front face were mixed with the Henschel mixer, and the toner (11) of the contents shown in Table 8 was obtained.

[0191] The example of toner manufacture 12 black fine-particles (5) 100 section and the titanium oxide impalpable powder 0.35 section used in the example 8 of toner manufacture were mixed with the Henschel mixer, and the toner (12) of the contents shown in Table 8 was obtained.

[0192] The example of toner manufacture 13 black fine-particles (5) 100 section and the anatase mold titanium oxide impalpable powder (whenever [ BET specific surface area  $100\text{m}^2/\text{g}$  and hydrophobing ] 61%, mean particle diameter of 0.05 micrometers) 1.5 section which carried out hydrophobing processing of the front face were mixed with the Henschel mixer, and the toner (13) of the contents shown in Table 8 was obtained.

[0193] The example 14 of toner manufacture, the 15 black fine-particles (5) 100 section, and the gamma-alumina impalpable powder (whenever [ BET specific surface area  $170\text{m}^2/\text{g}$  and hydrophobing ] 67%, mean particle diameter of 0.03 micrometers) 1.5 section which carried out hydrophobing processing of the front face or the silica impalpable powder (whenever [ BET specific surface area  $110\text{m}^2/\text{g}$  and hydrophobing ] 73%, mean particle diameter of 0.03 micrometers) 1.5 section was mixed with the Henschel mixer, and the toner (14) of the contents shown in Table 8 and (15) were obtained.

[0194] The example of toner manufacture 16 black fine-particles (6) 100 section and the amorphous mold titanium oxide impalpable powder 1.0 section used in the example 8 of toner manufacture were mixed with the Henschel mixer, and the toner (16) of the contents shown in Table 8 was obtained.

[0195] The example 17 of toner manufacture 25 black fine-particles (7) - (15) 100 section and the amorphous mold titanium oxide impalpable powder 1.5 section used in the example 8 of toner manufacture were mixed with the Henschel mixer, and toner [ of the contents shown in Table 8 ] (17) - (25) was obtained.

[0196]

[Table 8]

トナー 製造例 (トナーNo.)	使用した 黒色粉体 (黒色粉体No.)	粒径 ( $\mu\text{m}$ )	4 $\mu\text{m}$ 以下 粒子含有量 (%)	酸価 (KOH me/g)	Tg ( $^{\circ}\text{C}$ )	10%软化 温度 ( $^{\circ}\text{C}$ )	トナー樹脂の 溶解度 ポリマー (1/cm <sup>3</sup> ) <sup>12</sup>	外 添 剤					
								種類	粒径 ( $\mu\text{m}$ )	BET比表面積 ( $\text{B}$ )	疎水化度 (%)	外添量 (-A)	A×B
8	5	7	21	15	62	110	23.1	アセチン酸化チタン	0.03	130m <sup>2</sup> /g	71	1.5重量%	195
9	5	7	20	15	62	110	23.1	アセチン酸化チタン	0.03	130	71	2.5	325
10	5	7	19	15	62	110	23.1	アセチン酸化チタン	0.04	91	80	1.5	137
11	5	7	19	15	62	110	23.1	アセチン酸化チタン	0.04	87	73	1.5	131
12	5	7	20	15	62	110	23.1	アセチン酸化チタン	0.03	130	71	0.35	46
13	5	7	21	15	62	110	23.1	アセチン酸化チタン	0.05	100	61	1.5	150
14	5	7	21	15	62	110	23.1	ケーパシタ	0.03	170	87	1.5	255
15	5	7	20	15	62	110	23.1	シリカ	0.03	110	73	1.5	185
16	6	10	3	15	62	110	23.1	アセチン酸化チタン	0.02	130	71	1.0	130
17	7	7	18	0.8	61	103	21.6	アセチン酸化チタン	0.02	130	71	1.5	195
18	8	7	22	35	59	116	24.4	アセチン酸化チタン	0.02	130	71	1.5	195
19	9	7	18	15	41	75	22.9	アセチン酸化チタン	0.02	130	71	1.5	195
20	10	7	17	13	72	127	22.6	アセチン酸化チタン	0.02	130	71	1.5	195
21	11	7	19	15	62	111	22.9	アセチン酸化チタン	0.02	130	71	1.5	195
22	12	7	21	13	61	114	18.2	アセチン酸化チタン	0.02	130	71	1.5	195
23	13	7	19	0	67	118	18.8	アセチン酸化チタン	0.02	130	71	1.5	195
24	14	8.6	13	15	61	110	23.1	アセチン酸化チタン	0.02	130	71	1.5	195
25	15	8.8	5	15	62	110	23.1	アセチン酸化チタン	0.02	130	71	1.5	195

[0197] Mix a carrier (19) with example 22 toner (8) at 7% of toner concentration, and a developer is produced. Color copying machine CLC-500 (Canon make) is used as image formation equipment shown in drawing 3. Under 20 degrees C / 10% of environment, first, using the original manuscript of 25% of rates of image surface ratio, 10000-sheet \*\*\*\*\* was performed and 10000 more sheet \*\*\*\*\* was continuously performed using the original manuscript of 5% of rates of image surface ratio. Together with the following examples of an experiment, a result is shown in Table 9. As shown in Table 9, the above-mentioned developer also had little amount change of electrifications in \*\*\*\*\*-proof, and degradation of an image property, and the result which shows the very good endurance as which neither

SUPENTO nor toner scattering is also regarded was obtained.

[0198] When the same experiment as an example 22 was conducted using example 23 toner (9) and the carrier (19), a fall and slight aggravation of fogging were seen for the amount of electrifications a little with durability, and some carrier SUPENTO was seen in the SEM observation on the front face of a carrier after durability. Although it was possible that the reverse reaction of the restoration reaction of covering resin becomes easy to advance since the value of \*\*\*\* outside BET specific surface area  $\times$  of an external additive was as high as 325, it was the level which is satisfactory practically.

[0199] When the same experiment as an example 22 was conducted using example 24 toner (10) and the carrier (19), the amount of electrifications rose a little with durability, and image concentration fell slightly. Moreover, some carrier SUPENTO was seen in the SEM observation on the front face of a carrier after durability. Although it was considered since whenever [ hydrophobing / of an external additive ] was high, it was the level which is satisfactory practically.

[0200] When the same experiment as an example 22 was conducted using example 25 toner (11) and the carrier (19), a fall and slight aggravation of fogging were seen for the amount of electrifications a little with durability, and some carrier SUPENTO was seen in the SEM observation on the front face of a carrier after durability. the BET specific surface area of an external additive -- although it was possible that the restoration reaction of covering resin is small since it was small, it was the level which is satisfactory practically.

[0201] When the same experiment as an example 22 was conducted using example 26 toner (12) and the carrier (19), a fall and slight aggravation of fogging were seen for the amount of electrifications a little with durability, and some carrier SUPENTO was seen in the SEM observation on the front face of a carrier after durability. Although it was possible that the restoration reaction of covering resin is small since the value of \*\*\*\* outside BET specific surface area  $\times$  of an external additive was as small as 46, it was the level which is satisfactory practically.

[0202] When the same experiment as an example 22 was conducted using example 27 toner (13) and the carrier (19), a fall and slight aggravation of fogging were seen for the amount of electrifications a little with durability, and some carrier SUPENTO was seen in the SEM observation on the front face of a carrier after durability. The external additive was anatase mold titanium, and although it was possible that the crystal structure, therefore anionic polymerization catalyst ability are not high, it was the level which is satisfactory practically.

[0203] When the same experiment as an example 22 was conducted using example 28 toner (14) and the carrier (19), as shown in Table 9, the very good result was obtained.

[0204] When the same experiment as an example 22 was conducted using example 29 toner (8) and the carrier (20), as shown in Table 9, the very good result was obtained.

[0205] When the same experiment as an example 22 was conducted using example 30 toner (8) and the carrier (21), while the fall of the some of the amount of electrifications and slight aggravation of fogging were seen with durability and some carrier SUPENTO was seen in the SEM observation on the front face of a carrier after durability, some toner scattering was also looked at by the inside of a plane. Although it was considered that the covering condition of polyethylene resin is uneven, that the frictional electrification condition of a toner is not still more uniform, etc. since the covering approach of a carrier was the wet coat method, it was the level which is satisfactory practically.

[0206] When the carrier (22) was mixed with example 31 toner (8) at 5% of toner concentration, the developer was produced and the same experiment as an example 22 was conducted, the fall of the some of the amount of electrifications and slight aggravation of fogging were seen with durability, and some toner scattering was looked at by the after [ durability ] inside of a plane. Although it thought because the electrification rate is inadequate since carrier surface area was small, it was the level which is satisfactory practically.

[0207] When the same experiment as an example 22 was conducted using example 32 toner (8) and the carrier (23), some carrier SUPENTO was seen in the SEM observation on the front face of a carrier after durability. Although it thought since the toner which is hard to be developed since resistance of a carrier is too high stayed on the long duration carrier, it was the level which is satisfactory practically.

[0208] When the same experiment as an example 22 was conducted using example 33 toner (8) and the carrier (24), although some fogging also got worse, the result which shows the endurance which is satisfactory practically was well obtained by the image quality of the image obtained since resistance of a carrier was too low.

[0209] When the same experiment as an example 22 was conducted using example 34 toner (8) and the carrier (25), some carrier SUPENTO was seen in the SEM observation on the front face of a carrier after durability. Although it thought since the saturation magnetization of a carrier was too high, and developer degradation at the time of mixing within a development counter was promoted, it was the level which is satisfactory practically.

[0210] When the same experiment as an example 22 was conducted using example 35 toner (8) and the carrier (26), in addition to some carrier adhesion, the amount of electrifications fell a little with durability, and some toner scattering was looked at by the after [ durability ] inside of a plane. Although it was thought that it was because mixing with a developer and a supply toner is inadequate since the saturation magnetization of a carrier was too low, it was the level which is satisfactory practically.

[0211] When the carrier (19) was mixed with example of reference 4 toner (16) at 9% of toner concentration, the developer was produced and the same experiment as an example 22 was conducted, endurance was good, but since toner particle size was large, image quality was not so good through durability.

[0212] When the same experiment as an example 22 was conducted using example 36 toner (17) and the carrier (19), the amount of electrifications fell a little with durability, and some toner scattering was looked at by the after [ durability ] inside of a plane with aggravation of some of fogging. Although it thought because the electrification rate is slow since the acid number of a toner was low, it was the level which is satisfactory practically.

[0213] When the same experiment as an example 22 was conducted using example 37 toner (18) and the carrier (19), the amount of electrifications fell a little with durability, and some toner scattering was looked at by aggravation of fogging, and the after [ durability ] inside of a plane. Although it thought since the charge on a toner was revealed since the acid number of a toner was high, and the amount of electrifications fell, it was the level which is satisfactory practically.

[0214] When the same experiment as an example 22 was conducted using example 38 toner (19) and the carrier (19), the amount of electrifications fell a little with durability, some toner scattering was looked at by aggravation of fogging, and the after [ durability ] inside of a plane, and some carrier SUPENTO was further seen in the SEM observation on the front face of a carrier after durability. Although it thought because the degradation-proof nature of a toner is low since the temperature which shows Tg of a toner and the viscosity of 105  $\text{poises}$  was low, it was the level which is satisfactory practically.

[0215] Although fixable [ of a toner ] became it is bad and lower [ image concentration ] since the temperature which shows Tg of a toner and the viscosity of 105  $\text{poise}$  was high when the same experiment as an example 22 was conducted using example 39 toner (20) and the carrier (19), the result which shows very good endurance was obtained.

[0216] Although the amount of electrifications fell a little with durability, some toner scattering was looked at by aggravation of fogging, and the after [ durability ] inside of a plane and some carrier SUPENTO was further seen in the SEM observation on the front face of a carrier after durability when the same experiment as an example 22 was conducted using example 40 toner (21) and the carrier (19), it was the level which is satisfactory practically.

[0217] When the same experiment as an example 22 was conducted using example 41 toner (22) and the carrier (19), as shown in Table 9, the very good result was obtained.

[0218] When the same experiment as an example 22 was conducted using example 42 toner (23) and the carrier (19), the amount of electrifications fell a little with durability, some toner scattering was looked at by aggravation of fogging, and the after [ durability ] inside of a plane, and some carrier SUPENTO was further seen in the SEM observation on the front face of a carrier after durability. Since the solubility parameter of the resin used for manufacture of a toner was low, although considered for

compatibility with the polyethylene resin which is carrier coat resin to be high, and for a carrier to become easy SUPENTO, it was the level which is satisfactory practically.

[0219] When the carrier (19) was mixed with example 43 toner (24) at 9% of toner concentration, the developer was produced and the same experiment as an example 22 was conducted, image quality and endurance were good.

[0220] When the carrier (19) was mixed with example of reference 5 toner (25) at 9% of toner concentration, the developer was produced and the same experiment as an example 22 was conducted, endurance was good, but since there were few toner particles 4 micrometers or less, deterioration of image quality was seen.

[0221] Except making example 44 toner concentration into 1%, when the same experiment as an example 22 was conducted, degradation of image quality was remarkable, but other endurance was very good as shown in Table 9.

[0222] Except making example 45 toner concentration into 16%, when the same experiment as an example 22 was conducted, fogging was the level which is satisfactory practically not much well although some toner scattering was looked at by the after [ durability ] inside of a plane.

[0223] When the same experiment as an example 22 was conducted using the non coat article and toner (8) of ferrite impalpable powder which were used in the example 19 of example of comparison 1 carrier manufacture, the amount of electrifications fell with durability and aggravation of fogging, toner scattering inside the plane after durability, and carrier SUPENTO were seen.

[0224] When the same experiment as an example 22 was conducted using example of reference 6 toner (15), and the carrier (19), the amount of electrifications fell with durability and aggravation of fogging, toner scattering inside the plane after durability, and carrier SUPENTO were seen. When a hydrophobing processing silica without polymerization catalyst ability is used as an external additive, the wear or peeling of an enveloping layer by durability are not restored, but since carrier SUPENTO occurred and grew up to be the carrier surface part which deteriorated, it thinks.

[0225]

[Table 9]

	1177 (No.)	1178 (No.)	1179 (%)	帯電量(-nC/kg)			マクベス画像濃度			カブリ濃度 (%)			1180 (耐久後)	1181 (SEM観察)	1182 (初期)
				初期	25%原稿 10%後	5%原稿 10%後	初期	25%原稿 10%後	5%原稿 10%後	初期	25%原稿 10%後	5%原稿 10%後			
実施例22	19	8	7	38	38	34	1.66	1.67	1.65	0.4	0.5	0.4	○	○	○
実施例23	19	9	7	33	31	29	1.67	1.69	1.72	0.4	0.5	0.5	○	△	○
実施例24	19	10	7	32	33	38	1.68	1.66	1.52	0.4	0.4	0.3	○	△	○
実施例25	19	11	7	32	30	28	1.67	1.71	1.75	0.4	0.6	0.8	○	△	○
実施例26	19	12	7	34	31	29	1.62	1.68	1.71	0.3	0.7	0.9	○	△	○
実施例27	19	13	7	31	29	28	1.67	1.70	1.73	0.4	0.6	0.9	○	△	○
実施例28	19	14	7	32	32	33	1.68	1.69	1.67	0.4	0.5	0.4	○	○	○
実施例29	20	8	7	31	31	32	1.68	1.69	1.68	0.4	0.5	0.5	○	○	○
実施例30	21	8	7	28	26	24	1.71	1.73	1.80	0.6	0.8	1.0	△	△	○
実施例31	22	8	5	30	26	25	1.68	1.75	1.72	0.5	0.7	1.0	△	○	○
実施例32	23	8	7	34	31	30	1.48	1.54	1.58	0.4	0.7	0.8	○	△	○
実施例33	24	8	7	33	31	29	1.74	1.76	1.77	0.8	0.8	0.8	○	○	○
実施例34	25	8	7	34	31	28	1.64	1.68	1.73	0.4	0.6	0.8	○	△	○
実施例35	26	8	7	30	26	25	1.70	1.74	1.80	0.5	0.8	0.9	△	○	○
参考例 4	19	16	9	31	31	32	1.51	1.53	1.50	0.4	0.6	0.5	○	○	△
実施例36	19	17	7	33	29	26	1.68	1.78	1.83	0.4	0.9	1.0	△	○	○
実施例37	19	18	7	31	28	24	1.69	1.76	1.87	0.5	0.8	1.0	△	○	○
実施例38	19	19	7	33	28	26	1.66	1.77	1.82	0.4	0.9	1.0	△	△	○
実施例39	19	20	7	33	33	33	1.49	1.48	1.47	0.4	0.6	0.5	○	○	○
実施例40	19	21	7	32	30	27	1.68	1.69	1.73	0.4	0.8	0.9	△	△	○
実施例41	19	22	7	31	31	32	1.70	1.71	1.69	0.4	0.4	0.5	○	○	○
実施例42	19	23	7	30	28	25	1.71	1.73	1.75	0.4	0.8	1.0	△	△	○
実施例43	19	24	8	31	30	30	1.60	1.62	1.59	0.4	0.6	0.8	○	○	○
参考例 5	19	25	8	30	28	28	1.61	1.64	1.57	0.5	0.8	1.1	○	○	△
実施例44	19	8	7	44	45	49	0.41	0.39	0.27	0.2	0.1	0.1	○	○	○
実施例45	19	8	16	29	26	24	1.91	1.90	2.02	1.0	1.8	2.8	△	○	○
比較例 1	19-17 (34)	8	7	25	20	16	1.78	1.91	2.00	1.1	2.2	10.8	×	×	△
参考例 6	19	15	7	37	30	20	1.51	1.71	1.88	0.4	1.1	3.7	×	×	○

front Naka O: -- very much -- Good \*\*: -- practically with no problem Those with x:problem [0226]  
[Effect of the Invention] The carrier of this invention has a quick electrification rate, and has the high amount grant ability of electrifications and endurance, and the developer for electrophotography which used this carrier can show the outstanding endurance, and can maintain a good image property to stability.

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[Translation done.]